Supplementary Information

Optimization of Xantphos-type ligands for highly linear-selective hydroformylation of allyl alcohol and alkenes

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1. Chemicals and materials

Air- and moisture-sensitive manipulations were conducted using standard Schlenk techniques. Unless otherwise specified, all commercially available reagents were utilized without further purification.

1-Naphthol, palladium(II) acetate ($Pd(OAc)_2$), triphenylphosphine (PPh_3), cesium carbonate (Cs_2CO_3), *N*,*N*-dimethylformamide (DMF), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA), chlorodiphenylphosphine (PPh_2Cl), super-dehydrated diethyl ether (Et_2O), 4,6-bis(diphenylphosphino)phenoxazine (Nixantphos, **L2**), sodium hydride (NaH), benzyl chloride, super-dehydrated tetrahydrofuran (THF), diethylamine (Et_2NH), concentrated hydrochloric acid (HCl), super-dehydrated toluene, 1-decene (**1d**), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos, **L1**), nonanal (**2c**), and undecanal (**2d**) were procured from FUJIFILM Wako Pure Chemical Corporation.

1,2-Dibromobenzene, phosphorus trichloride (PCl_3), 5-bromo-*m*-xylene, carbonylhydridotris(triphenylphosphine)rhodium(I) ($RhH(CO)(PPh_3)_3$), styrene (**1e**), 3-buten-1-ol (**1f**), allylbenzene (**1g**), allyl acetate (**1h**), heptanal (**1b**), octanal, and 3-phenylpropanal (**2e**) were sourced from Tokyo Chemical Industry Co., Ltd.

Butyllithium (BuLi, 2.5 M in hexane), phenoxazine, *tert*-butyldimethylchlorosilane ((*t*-Bu)Me_2SiCl), and tetrabutylammonium fluoride trihydrate ($Bu_4NF{\cdot}3H_2O$) were obtained from Sigma-Aldrich.

1-Hexene (**1b**) and 1-octene (**1c**) were purchased from Kanto Chemical Co., Inc. Allyl alcohol (**1a**) was supplied by Showa Denko K.K. (currently Crasus Chemical Inc.). H_2 (99.995 vol%; Fukuoka Oxygen Co., Ltd.) and CO (99.95%; Sumitomo Seika Chemicals Co., Ltd.) were used as received.

Elemental analyses were conducted at the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 spectrometer at the Evaluation Center of Materials Properties and Function, Institute for Materials Chemistry and Engineering, Kyushu University.

2. Instruments

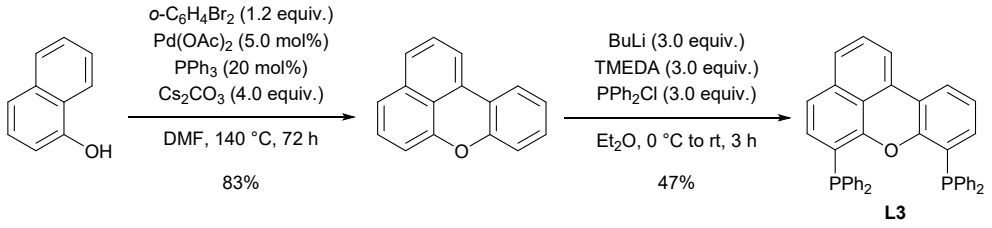
^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 spectrometer. Chloroform-*d* ($CDCl_3$) containing 0.03% tetramethylsilane (TMS) was used as the solvent. Chemical shifts are reported in ppm and referenced to TMS (0.00 ppm) for ^{1}H NMR and to the residual $CDCl_3$ signal (77.16 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), integration, and assignment. For ^{13}C NMR spectra of phosphine ligands, inverse-gated proton decoupling with nuclear Overhauser effect (NOE) suppression and a long relaxation delay (60 s) were employed to enable quantitative integration. This approach was employed because the ligands contain multiple aromatic rings, resulting in low ^{13}C sensitivity, and because significant ^{13}C–^{31}P coupling can complicate signal intensities.

Conversions and product yields for the hydroformylation of **1a** were determined through high-performance liquid chromatography (HPLC) using a Shodex SUGAR SH-1011 column (8.0 × 300 mm; Showa Denko K.K.) with a UV detector (210 nm) and a refractive index (RI) detector (JASCO) except for γ-butyrolactone (dihydrofuran-2(3*H*)-one, **6a**). Data acquisition and integration were performed using a Shimadzu C-R7A plus CHROMATOPAC system, and quantification was carried out using the absolute calibration method. The yield of **6a** was determined through gas chromatography (GC) on an Agilent 7890A equipped with a flame ionization detector (FID) and a J&W DB1701 column (30 m × 0.53 mm i.d., 1.0 μm film thickness), using the absolute calibration method.

Similarly, conversions and product yields for the hydroformylation of alkenes (**1b**–**1h**) were determined through GC on an Agilent 6850 Series II system equipped with a FID and a J&W HP-1 column (30 m × 0.32 mm i.d., 0.25 μm film thickness), using octanal or heptanal as the internal standard.

3. Synthesis of phosphine ligands

6,7-Bis(diphenylphosphino)benzo[k,l]xanthene (Benzoxantphos, L3)



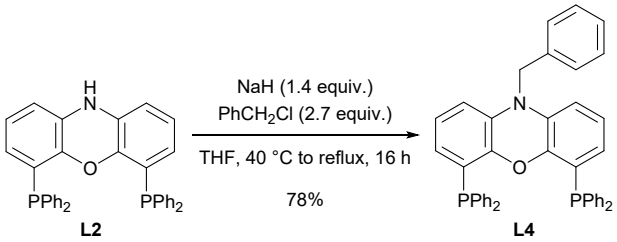
Benzo[k,l]xanthene was synthesized according to a reported procedure[1] with slight modifications. A nitrogen-purged 200 mL two-neck round-bottom flask was charged with Cs_2CO_3 (18.07 g, 55.5 mmol) and dried under vacuum at 150 °C for 2 h. After cooling, $Pd(OAc)_2$ (0.15 g, 0.70 mmol), PPh_3 (0.73 g, 2.77 mmol), 1-naphthol (2.0 g, 13.9 mmol), 1,2-dibromobenzene (2.0 mL, 16.6 mmol), and DMF (80 mL) were added. The mixture was refluxed at 140 °C for 72 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O and water, and the layers were separated. The organic layer was washed with water, dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford benzo[k,l]xanthene as a white solid (2.5 g, 83% yield).

L3 was then synthesized according to a reported procedure[2] with slight modifications. In a nitrogen-purged 200 mL three-neck round-bottom flask, benzo[k,l]xanthene (2.0 g, 9.13 mmol), TMEDA (4.1 mL, 27.5 mmol), and super-dehydrated Et_2O (100 mL) were combined. The mixture was cooled to 0 °C, and BuLi (2.5 M in hexane, 11 mL, 27.5 mmol) was added dropwise over 20 min. After stirring at room temperature for 16 h, the mixture was cooled again to 0 °C, and PPh_2Cl (4.9 mL, 27.4 mmol) was added. Stirring was continued at room temperature for 3 h. The reaction mixture was diluted with dichloromethane (CH_2Cl_2), and the layers were separated. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was washed with hexane and recrystallized from CH_2Cl_2/hexane to afford the desired compound as a pale yellow solid (2.5 g, 47% yield; 39% overall yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.25–7.15 (m, 21H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 8.2, 3.4 Hz, 1H), 6.63 (ddd, *J* = 7.6, 3.6, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$,

inverse-gated proton decoupling) δ = 153.9–153.6 (m, 2C), 137.4 (d, *J* = 13.4 Hz, 2C), 136.5 (d, *J* = 12.4 Hz, 2C), 135.4 (s, 1C), 134.5 (s, 1C), 133.9 (dd, *J* = 37.2, 20.0 Hz, 8C), 131.7 (s, 1C), 128.6–128.1 (m, 13C), 127.4 (t, *J* = 9.5 Hz, 2C), 125.8 (s, 1C), 123.9 (s, 1C), 123.5 (s, 1C), 121.2 (d, *J* = 2.8 Hz, 1C), 120.3 (d, *J* = 4.7 Hz, 2C), 115.8 (d, *J* = 18.1 Hz, 1C), 115.1 (s, 1C). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −17.4 (d, *J* = 21.7 Hz, 1P), −20.6 (d, *J* = 21.7 Hz, 1P). Elemental Analysis: Calcd for $C_{40}H_{28}OP_2$: C, 81.90; H, 4.81; N, 0.00. Found: C, 81.70; H, 4.82; N, 0.01.

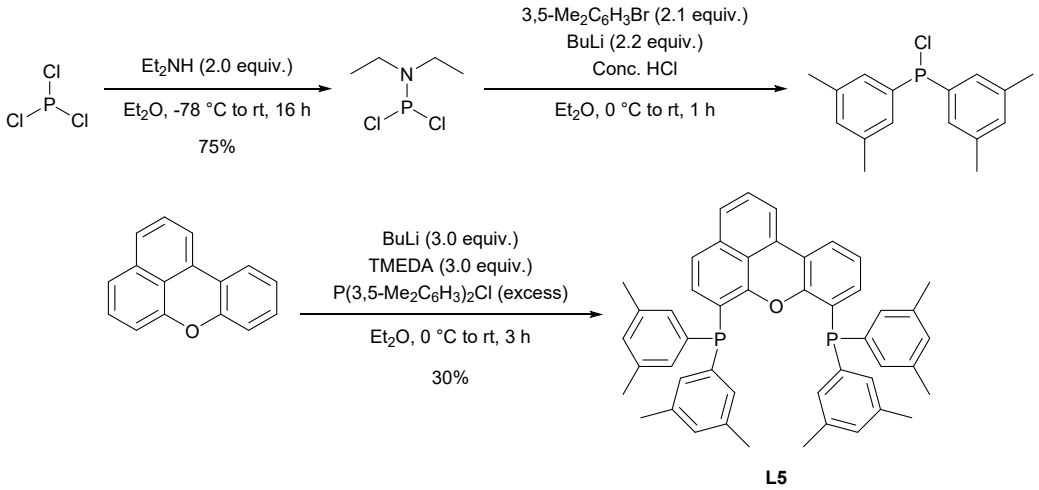
_N_-Benzyl-4,6-bis(diphenylphosphino)phenoxazine (_N_-Benzyl-Nixantphos, L4)



L4 was synthesized according to the reported procedure[2] with slight modifications. A nitrogen-purged 200 mL two-neck round-bottom flask was charged with **L2** (1.0 g, 1.81 mmol) and super-dehydrated THF (20 mL). NaH (0.10 g, 2.5 mmol) was added, and the mixture was refluxed at 40 °C for 1 h. A solution of benzyl chloride (0.62 g, 4.9 mmol) in THF (5.0 mL) was then added, and the mixture was refluxed at 70 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with benzene and brine, and the layers were separated. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was washed with hexane and recrystallized from CH_2Cl_2/ethanol (EtOH) to afford the desired compound as a pale gray solid (0.90 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37–7.27 (m, 5H), 7.25–7.20 (m, 20H), 6.56 (t, *J* = 7.8 Hz, 2H), 6.29 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.01 (dq, *J* = 7.9, 1.5 Hz, 2H), 4.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, inverse-gated proton decoupling) δ = 147.6 (t, *J* = 10.5 Hz, 2C), 137.0 (t, *J* = 6.2 Hz, 4C), 136.1 (s, 1C), 134.1–133.9 (m, 9C), 129.1 (s, 2C), 128.4–128.3 (m, 13C), 127.4 (s, 1C), 126.2 (s, 2C), 125.7 (s, 2C), 124.9–124.7 (m, 2C), 123.9 (s, 2C), 112.9 (s, 2C), 50.0 (s, 1C). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −18.4 (s, 2P). HRMS-FAB (*m*/*z*): $[M]^+$ calcd for $C_{43}H_{33}NOP_2$, 641.2037; found: 641.2016.

6,7-Bis[di(3,5-dimethylphenyl)phosphino]benzo[k,l]xanthene
(3,5-Xylyl-Benzoxantphos, L5)



Dichlorodiethylaminophosphine (Cl_2P-$N(Et)_2$) was synthesized according to the reported procedure[3] with slight modifications. A nitrogen-purged 500 mL three-neck round-bottom flask was charged with PCl_3 (4.3 mL, 50 mmol) and super-dehydrated Et_2O (300 mL). Et_2NH (10.4 mL, 100 mmol) was added dropwise at −78 °C over 30 min. The mixture was stirred at room temperature for 16 h and then filtered. The filtrate was distilled to remove the solvent, and the residue was purified by vacuum distillation to afford Cl_2P-$N(Et)_2$ as a colorless liquid (6.5 g, 75% yield).

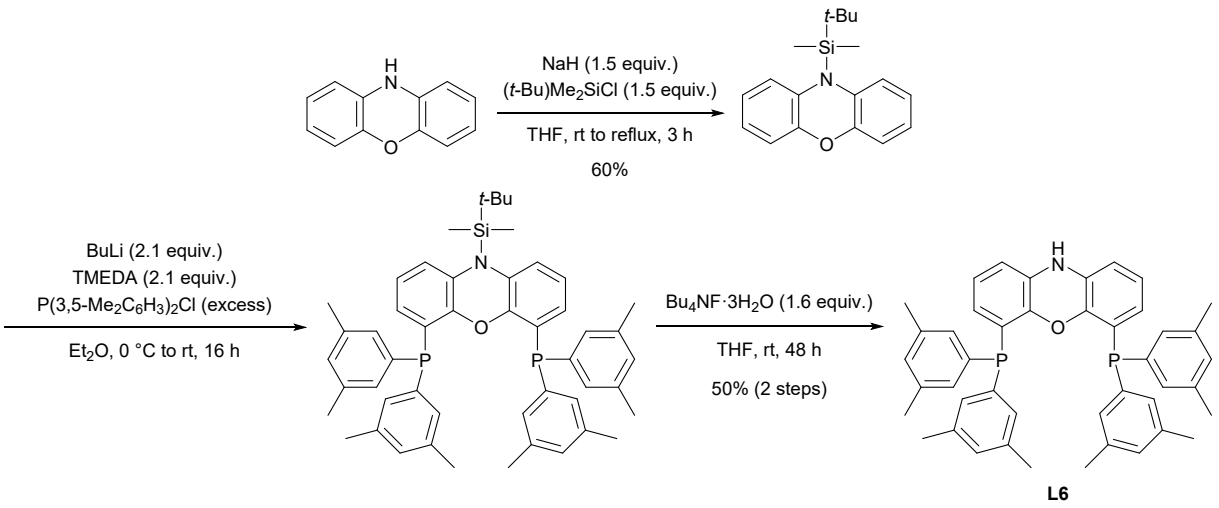
Bis(3,5-dimethylphenyl)chlorophosphine was synthesized according to the reported procedure[4] with slight modifications. A nitrogen-purged 500 mL three-neck round-bottom flask was charged with 5-bromo-*m*-xylene (25 g, 135 mmol) and super-dehydrated Et_2O (250 mL). The mixture was cooled to 0 °C, and BuLi (2.5 M in hexane, 88.4 mL, 142 mmol) was added dropwise over 20 min. After stirring at 0 °C for 4 h, Cl_2P-$N(Et)_2$ (11.19 g, 64.33 mmol) was added, and stirring was continued for another 4 h. Concentrated HCl (33 mL) was then added at 0 °C, and the mixture was stirred at room temperature for 1 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated and dried under reduced pressure for 24 h to afford bis(3,5-dimethylphenyl)chlorophosphine, which was directly used for the next step without further purification.

L5 was synthesized following a reported procedure[2] with slight modifications. A nitrogen-purged 200 mL three-neck round-bottom flask was charged with benzo[k,l]xanthene (2.0 g, 9.13 mmol), TMEDA (4.1 mL, 27.5 mmol), and super-dehydrated Et_2O (100 mL). The mixture was cooled to 0 °C, and BuLi (2.5 M in hexane,

11 mL, 27.5 mmol) was added dropwise over 20 min. After stirring at room temperature for 16 h, the mixture was cooled again to 0 °C, and bis(3,5-dimethylphenyl)chlorophosphine (excess) was added. Stirring was continued at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 and water, and the layers were separated. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was washed with hexane and recrystallized from CH_2Cl_2/hexane to afford the desired compound as a pale yellow solid (1.9 g, 30% yield; 25% overall yield over two steps from 1-naphthol).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.87–6.84 (m, 9H), 6.80 (d, *J* = 7.6 Hz, 4H), 6.70 (ddd, *J* = 7.4, 3.3, 1.1 Hz, 1H), 2.18 (d, *J* = 4.4 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, inverse-gated proton decoupling) δ = 154.1–153.8 (m, 2C), 137.7 (s, 1C), 137.5–137.3 (m, 9C), 136.5 (d, *J* = 12.4 Hz, 2C), 135.3 (s, 1C), 134.8 (s, 1C), 132.3 (s, 1C), 131.6 (dd, *J* = 49.1, 20.5 Hz, 8C), 130.2 (d, *J* = 37.1 Hz, 4C), 128.1–127.7 (m, 3C), 125.6 (s, 1C), 123.4 (d, *J* = 49.6 Hz, 2C), 121.3 (d, *J* = 2.9 Hz, 1C), 120.1 (s, 2C), 116.5 (d, *J* = 20.0 Hz, 1C), 114.8 (s, 1C), 21.5 (s, 8C). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −17.5 (d, *J* = 20.6 Hz, 1P), −21.2 (d, *J* = 20.6 Hz, 1P). HRMS-FAB (*m*/*z*): $[M]^+$ calcd for $C_{48}H_{44}OP_2$, 698.2867; found: 698.2864.

4,6-Bis[di(3,5-dimethylphenyl)phosphino]phenoxazine (3,5-Xylyl-Nixantphos, L6)



10-(*tert*-Butyldimethylsilyl)phenoxazine was synthesized according to the reported procedure[5] with slight modifications. A nitrogen-purged 200 mL two-neck round-bottom flask was charged with phenoxazine (5.0 g, 27.3 mmol) and super-dehydrated THF (80 mL). NaH (1.65 g, 41.3 mmol) was added, and the mixture was refluxed at 40 °C for 1 h. After cooling to room temperature, a solution of (*t*-Bu)Me_2SiCl (6.17 g, 40.9 mmol) in THF (10 mL) was added, and the reaction mixture was refluxed at 70 °C for at least 3 h. The mixture was then cooled to room temperature, quenched with ice water, and extracted with ethyl acetate (AcOEt). The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford 10-(*tert*-butyldimethylsilyl)phenoxazine as a white solid (2.5 g, 60% yield).

L6 was synthesized according to the reported procedure[2] with slight modifications. A nitrogen-purged 200 mL three-neck round-bottom flask was charged with 10-(*tert*-butyldimethylsilyl)phenoxazine (2.0 g, 6.73 mmol), TMEDA (1.6 mL, 14.1 mmol), and super-dehydrated Et_2O (100 mL). The mixture was cooled to 0 °C, and BuLi (2.5 M in hexane, 8.8 mL, 14.1 mmol) was added dropwise over 10 min. The mixture was stirred at room temperature for 16 h, cooled again to 0 °C, and bis(3,5-dimethylphenyl)chlorophosphine (excess) was added. The reaction mixture was stirred at room temperature for an additional 16 h. After quenching with water, the mixture was diluted with CH_2Cl_2 and water, and the layers were separated. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product as a solid.

The crude solid was dried and dissolved in THF (50 mL), followed by the addition of $Bu_4NF \cdot 3H_2O$ (3.4 g, 10.8 mmol). The mixture was stirred at room temperature for 48 h. After solvent removal under reduced pressure, the residue was diluted with CH_2Cl_2 and water, and the layers were separated. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and the residue was washed with hexane and EtOH. Recrystallization from CH_2Cl_2/EtOH afforded the desired compound as a pale gray solid (2.3 g, 50% yield from 10-(*tert*-butyldimethylsilyl)phenoxazine; 30% overall yield over three steps from phenoxazine).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.85 (s, 4H), 6.82–6.81 (m, 8H), 6.60 (t, J = 7.8 Hz, 2H), 6.33 (d, J = 7.2 Hz, 2H), 6.05 (s, 2H), 5.13 (s, 1H), 2.20 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, inverse-gated proton decoupling) δ = 146.0–145.7 (m, 2C), 137.3 (s, 8C), 136.8 (s, 4C), 131.9–131.4 (m, 11C), 130.2 (s, 4C), 126.1 (s, 3C), 123.6 (s, 2C), 113.6 (s, 2C), 21.5 (s, 8C). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −18.7 (s, 2P). Elemental Analysis: Calcd for $C_{44}H_{43}NOP_2$: C, 79.62; H, 6.53; N, 2.11. Found: C, 79.17; H, 6.56; N, 2.13. HRMS-FAB (m/z): $[M]^+$ calcd for $C_{44}H_{43}NOP_2$, 663.2820; found: 663.2809.

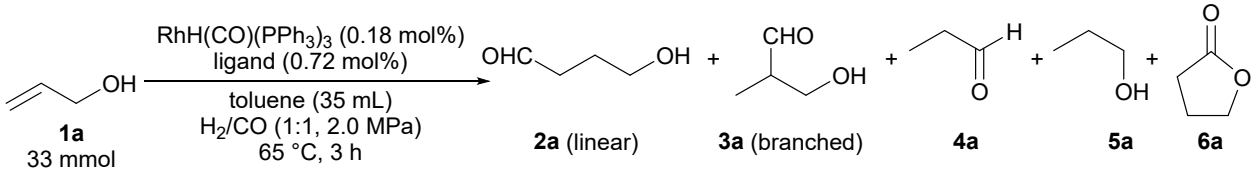
4. General procedure for the hydroformylation reactions

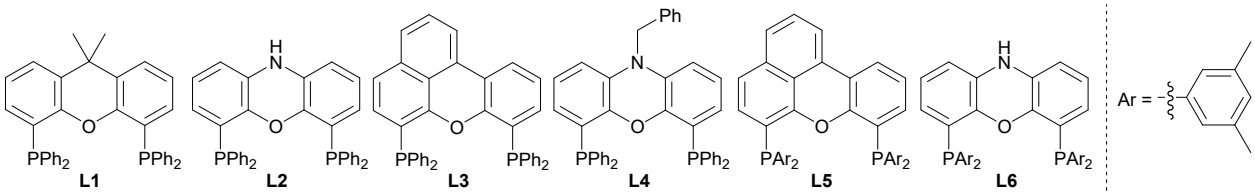
Hydroformylation of 1a. In a 100 mL stainless-steel autoclave equipped with an inner glass tube and a magnetic stirring bar, **1a** (1.9 g, 33 mmol), toluene (35 mL) as the solvent, $RhH(CO)(PPh_3)_3$ (54 mg, 58 μmol) as the catalyst, and phosphine ligands (0.23 mmol) were added. The autoclave was pressurized with a mixture of CO and H_2 to a total pressure of 2.0 MPa (CO: 1.0 MPa; H_2: 1.0 MPa) and stirred at 65 °C for 3 h. After completion, water (60 mL) was added, and the aqueous phase was separated by liquid–liquid extraction to give an aqueous solution containing the product. The mixture was analyzed by HPLC. Column: Shodex SUGAR SH-1011 (8.0 × 300 mm; Showa Denko K.K.). Conditions: column temperature, 40 °C; eluent, 0.01 N aqueous sulfuric acid (H_2SO_4); flow rate, 0.5 mL min^{-1}. Because 4-hydroxybutanal and 2-hydroxytetrahydrofuran exist in equilibrium in aqueous solution, the yield of **2a** (linear) was defined as the sum of the individual yields of both species, which appeared as a single peak in HPLC. Retention times were as follows: allyl alcohol (**1a**), 30.4 min; 4-hydroxybutanal and 2-hydroxytetrahydrofuran (**2a**, linear), 27.2 min; 3-hydroxy-2-methylpropanal (**3a**, branched), 25.3 min; propanal (**4a**), 31.2 min; propanol (**5a**), 37.5 min.

Hydroformylation of alkenes (1b–1h). In a 40 mL stainless-steel autoclave equipped with an inner glass tube and a magnetic stirring bar, $RhH(CO)(PPh_3)_3$ (5.5 mg, 6.0 μmol) and phosphine ligands (24 μmol) were added. Under an inert atmosphere, freeze-pump-thaw (FPT)-treated super-dehydrated toluene (3.0 mL) and FPT-treated alkenes (3.0 mmol) were introduced. The autoclave was purged with H_2 three times, then pressurized with a mixture of CO and H_2 to a total pressure of 2.0 MPa (CO: 1.0 MPa; H_2: 1.0 MPa) and stirred at 65 °C for 3 h. After cooling to room temperature, the pressure was carefully released. The crude mixture was analyzed by GC-FID using octanal or heptanal as an internal standard.

5. Computational mechanistic studies on the hydroformylation

Table S1. L/B ratios of the hydroformylation of **1a**, including byproducts, vs free energy differences for the 1,2- and 2,1-insertion pathways from DFT calculations (ligands **L1**–**L6**).

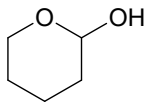




	L1	L2	L3	L4	L5	L6
2a (linear) (%)	84.7	85.2	88.3	84.4	90.3	91.8
3a (branched) (%)	5.9	6.5	6.0	6.9	6.7	6.7
4a (propanal) (%)	3.8	2.1	1.9	3.4	1.3	1.5
5a (propanol) (%)	1.6	1.5	0.8	1.1	0.3	0.9
6a (γ-butyrolactone) (%)	0.4	0.5	0.4	0.4	0.5	0.5
Mass balance (%)	96.4	95.8	97.4	96.2	99.1	101.4
L/B (**2a**/**3a**)	93.5/6.5 (14.4)	92.9/7.1 (13.1)	93.6/6.4 (14.7)	92.4/7.6 (12.2)	93.1/6.9 (13.5)	93.2/6.8 (13.7)
Total L/B: (**2a** + **6a**)/(**3a** + **4a**)	89.8/10.2 (8.8)	90.9/9.1 (10.0)	91.8/8.2 (11.2)	89.2/10.8 (8.2)	91.9/8.1 (11.4)	91.8/8.2 (11.3)
Total L/B: (**2a** + **6a**)/(**3a** + **4a** + **5a**)	88.3/11.7 (7.5)	89.5/10.5 (8.5)	91.1/8.9 (10.2)	88.1/11.9 (7.4)	91.6/8.4 (10.9)	91.0/9.0 (10.1)
1,2-Insertion $\Delta G‡$ (kcal mol^{-1})	15.4	16.2	18.5	18.4	15.7	16.5
2,1-Insertion $\Delta G‡$ (kcal mol^{-1})	20.2	20.6	23.4	22.0	22.6	23.1
$\Delta\Delta G‡$ (kcal mol^{-1})	4.8	4.4	4.9	3.6	6.9	6.6

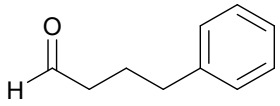
6. Characterization of products

2-Hydroxytetrahydropyran (2f)



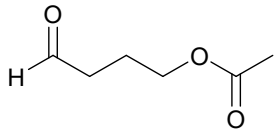
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.90–4.89 (m, 1H), 4.04–3.99 (m, 1H), 3.75–3.74 (m, 1H), 3.56–3.51 (m, 1H), 1.88–1.77 (m, 2H), 1.53–1.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 94.6, 64.0, 32.0, 25.3, 20.4. Elemental Analysis: Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87; N, 0.00. Found: C, 58.75; H, 9.91; N, 0.04.

4-Phenylbutanal (2g)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.75 (t, *J* = 1.6 Hz, 1H), 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.45 (td, *J* = 7.2, 1.6 Hz, 2H), 1.97 (quin, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.5, 141.3, 128.6, 126.2, 43.2, 35.1, 23.7. Elemental Analysis: Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16; N, 0.00. Found: C, 80.44; H, 8.15; N, 0.13. HRMS-FAB (*m*/*z*): $[M-H]^+$ calcd for $C_{10}H_{11}O$, 147.0810; found: 147.0822.

4-Acetoxybutanal (2h)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.80 (t, *J* = 1.2 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 2H), 2.56 (td, *J* = 6.8, 1.2 Hz, 2H), 2.06 (s, 3H), 1.98 (quin, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.4, 171.2, 63.5, 40.6, 21.4, 21.0. Elemental Analysis: Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; N, 0.00. Found: C, 54.81; H, 7.69; N, 0.00. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_6H_{11}O_3$, 131.0708; found: 131.0708.

7. ^{1}H, ^{13}C, and ^{31}P NMR spectra and GC-FID chromatograms

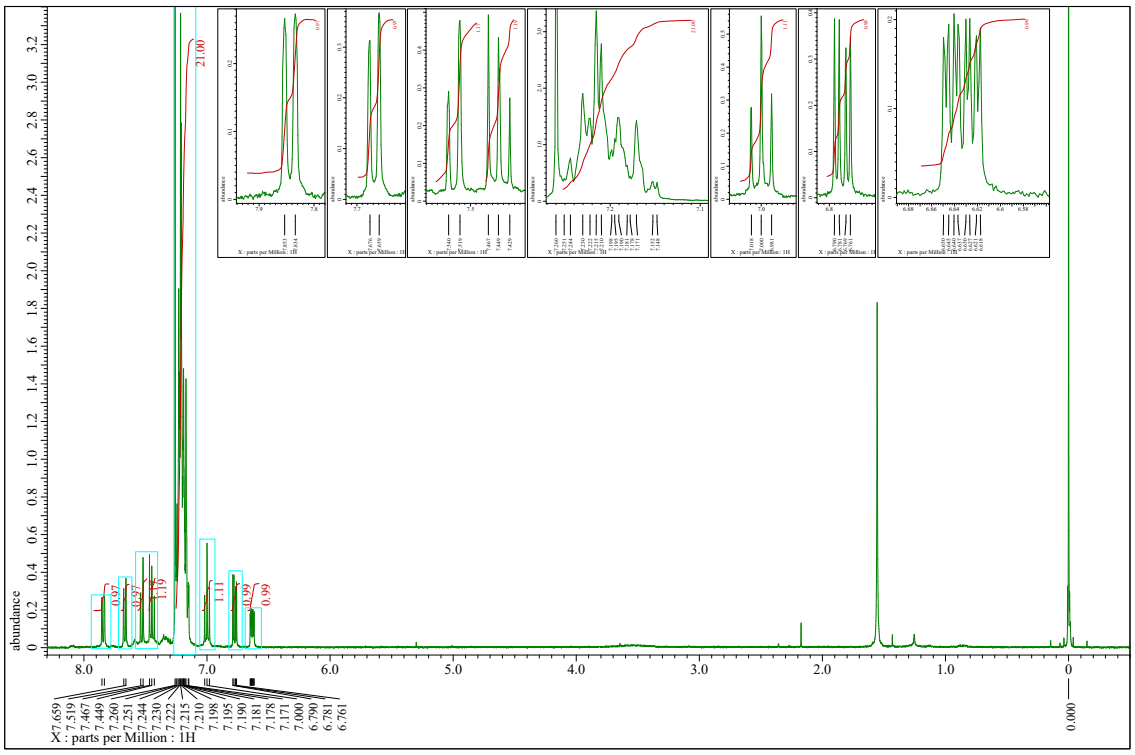


Fig. S1. ^{1}H NMR spectra of Benzoxantphos (**L3**) in $CDCl_3$.

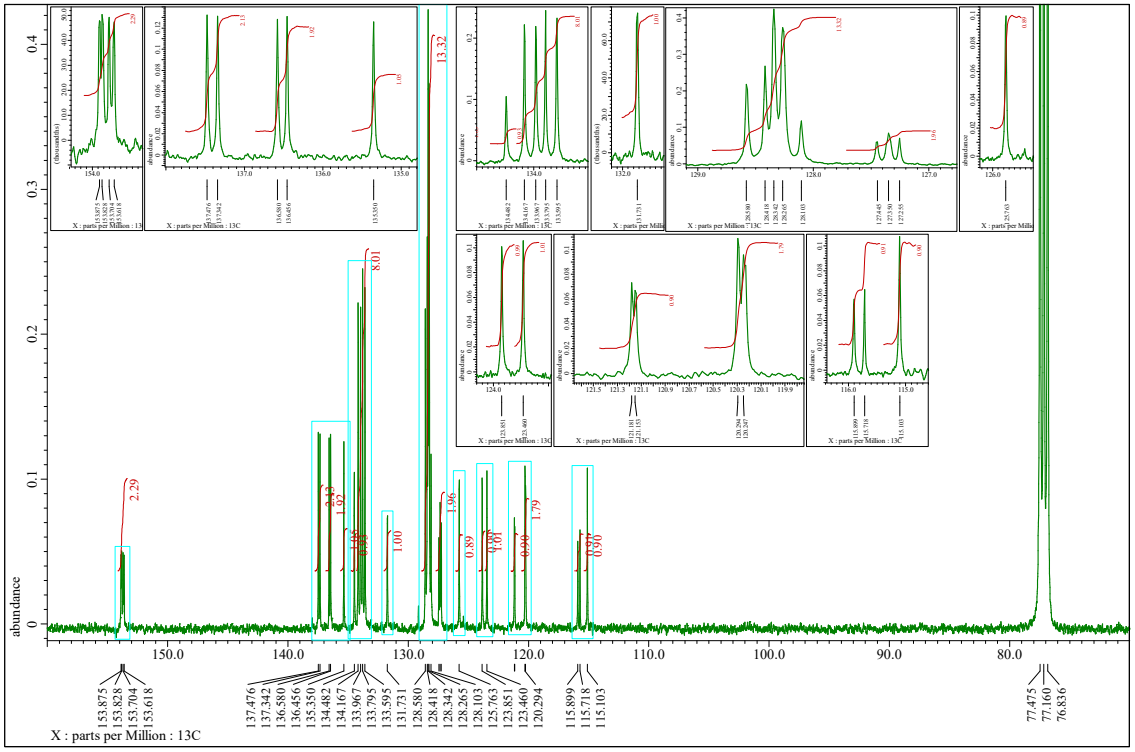


Fig. S2. ^{13}C NMR spectra of Benzoxantphos (**L3**) in $CDCl_3$ (inverse-gated proton decoupling).

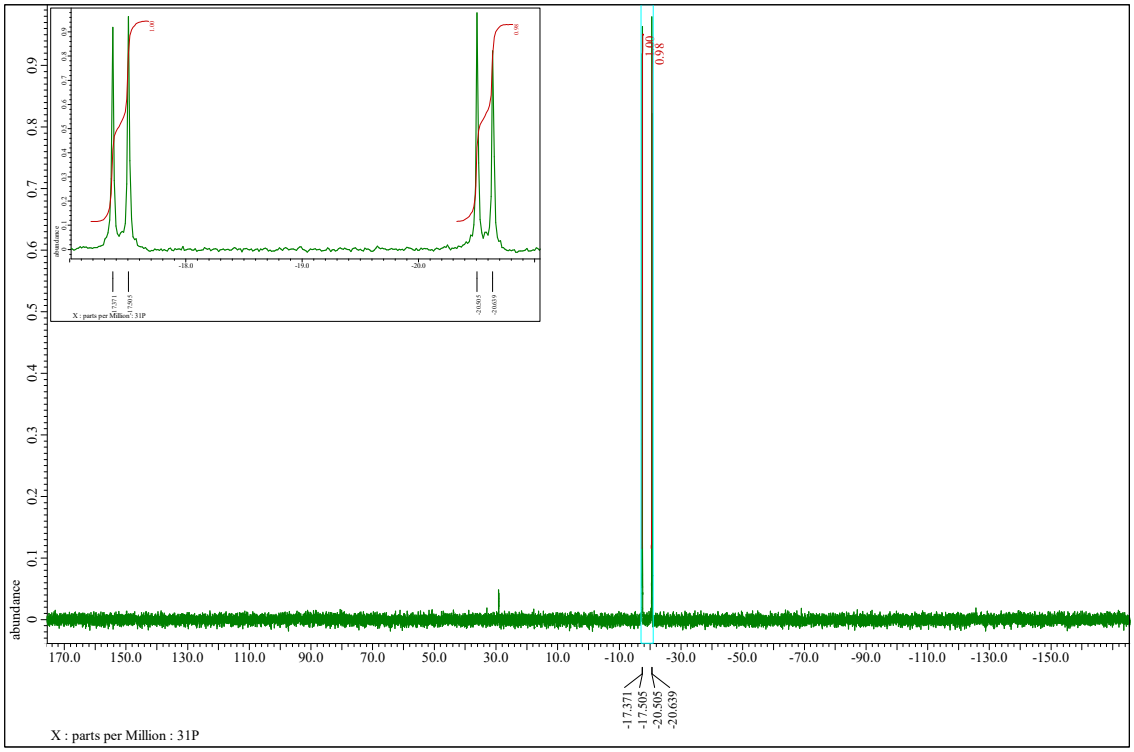


Fig. S3. ^{31}P NMR spectra of Benzoxantphos (**L3**) in $CDCl_3$.

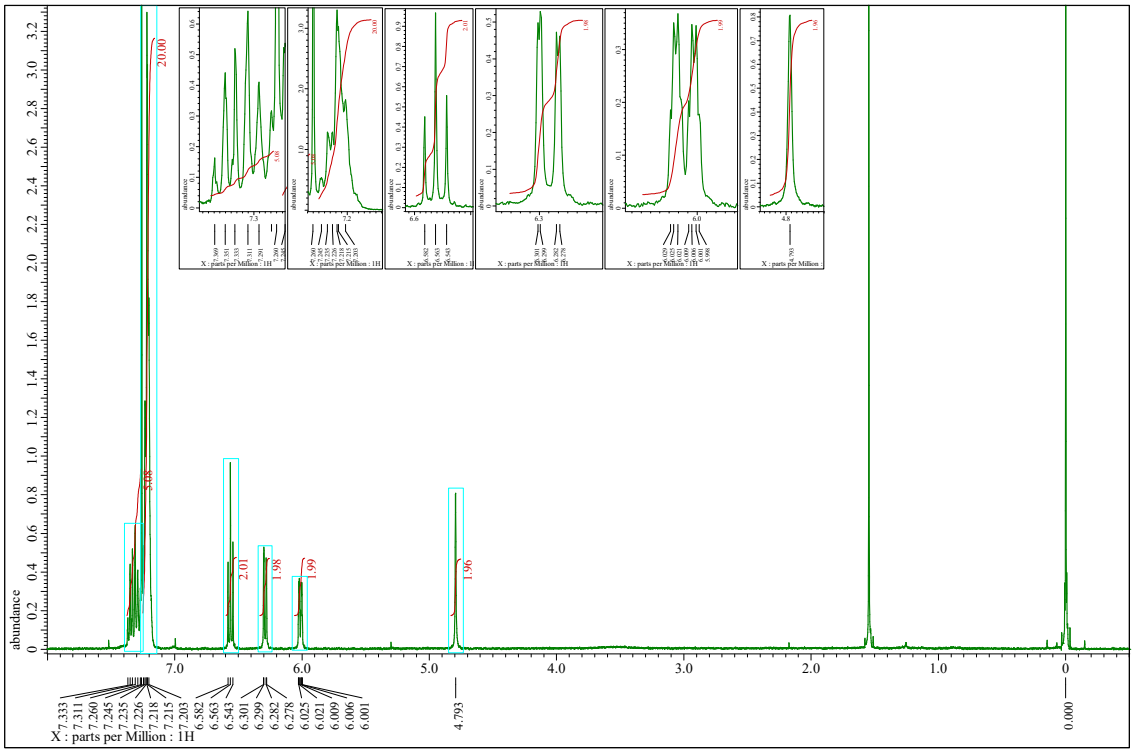


Fig. S4. ^{1}H NMR spectra of *N*-benzyl-Nixantphos (**L4**) in $CDCl_3$.

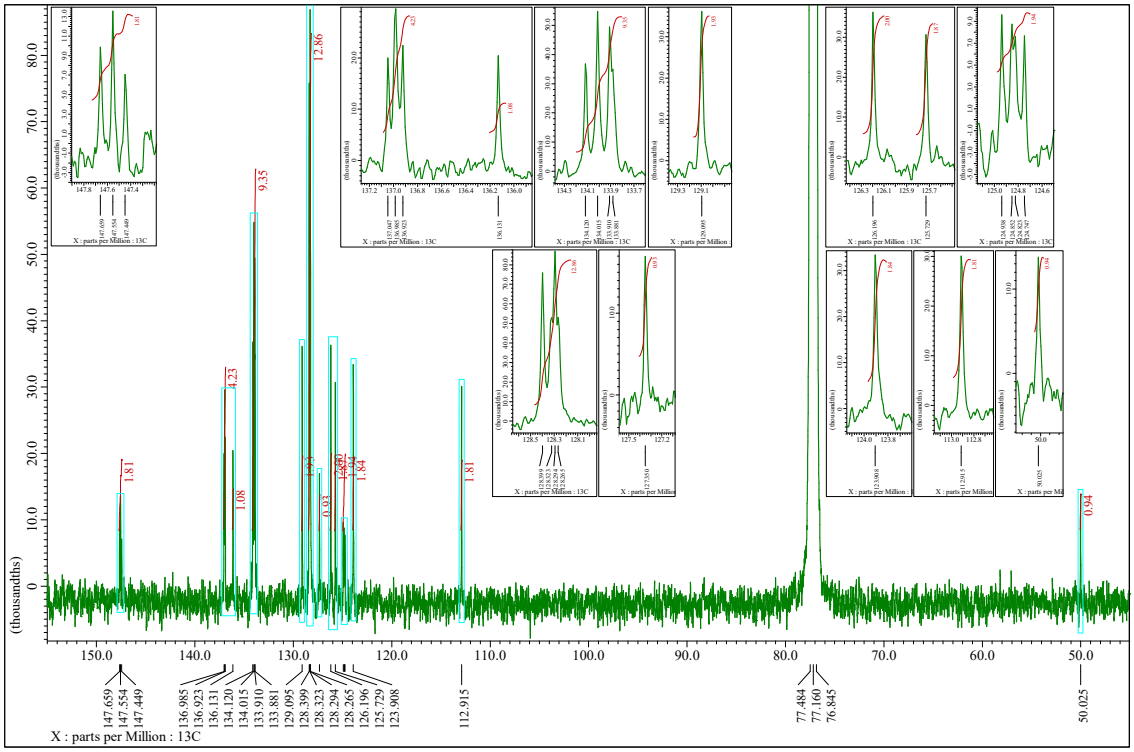


Fig. S5. ^{13}C NMR spectra of *N*-benzyl-Nixantphos (**L4**) in $CDCl_3$ (inverse-gated proton decoupling).

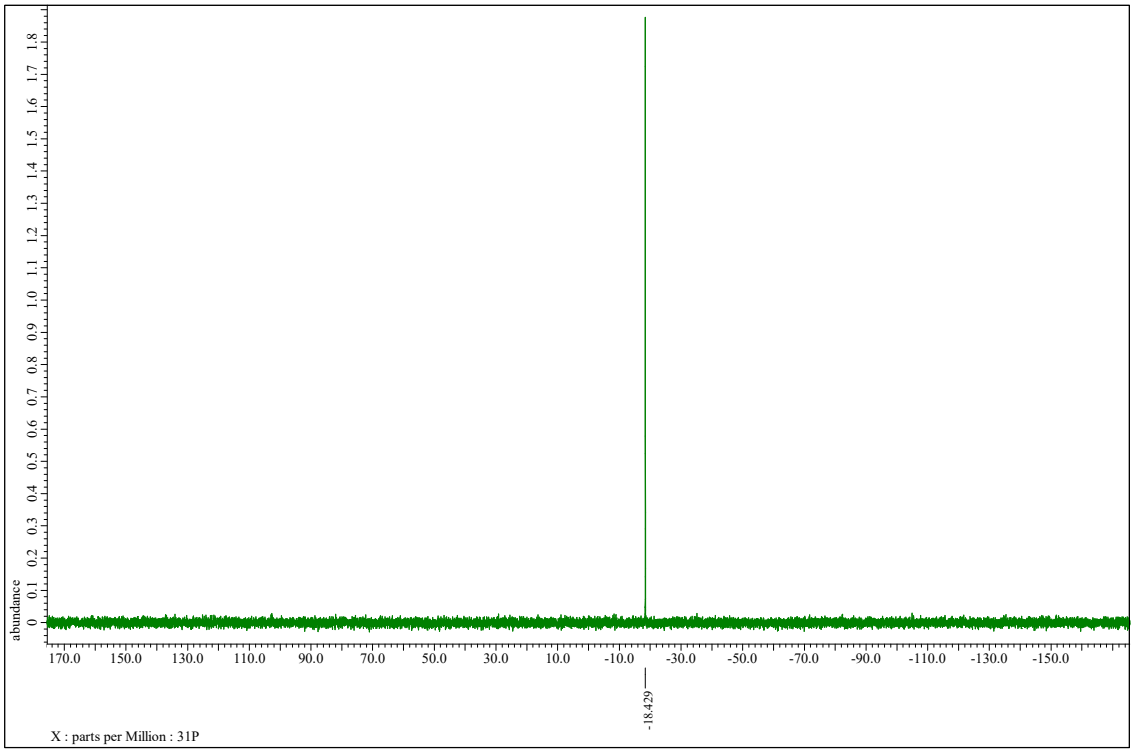


Fig. S6. ^{31}P NMR spectra of *N*-benzyl-Nixantphos (**L4**) in $CDCl_3$.

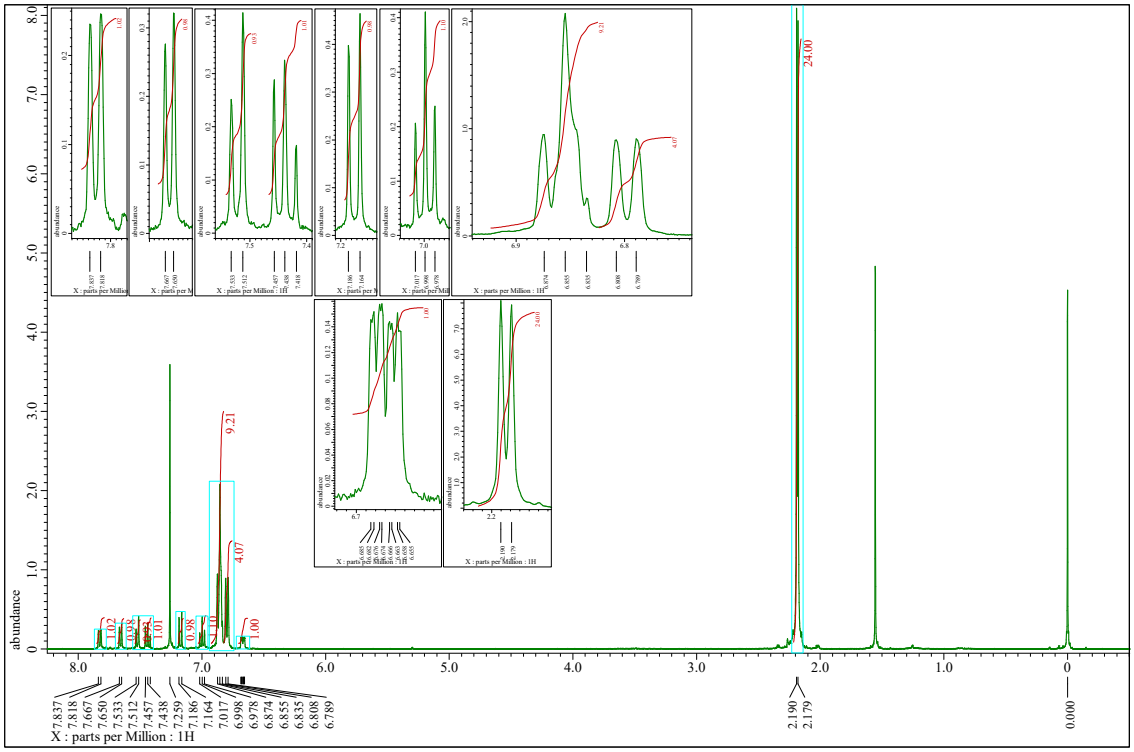


Fig. S7. ^{1}H NMR spectra of 3,5-xylyl-Benzoxantphos (**L5**) in $CDCl_3$.

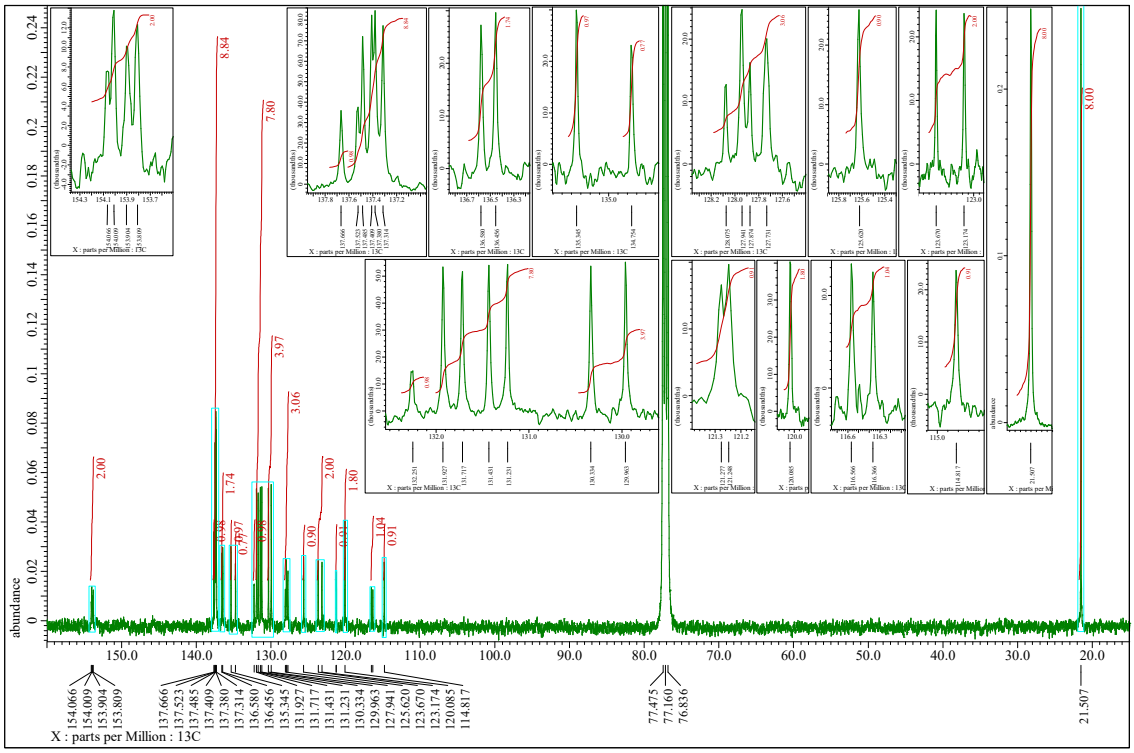


Fig. S8. ^{13}C NMR spectra of 3,5-xylyl-Benzoxantphos (**L5**) in $CDCl_3$ (inverse-gated proton decoupling).

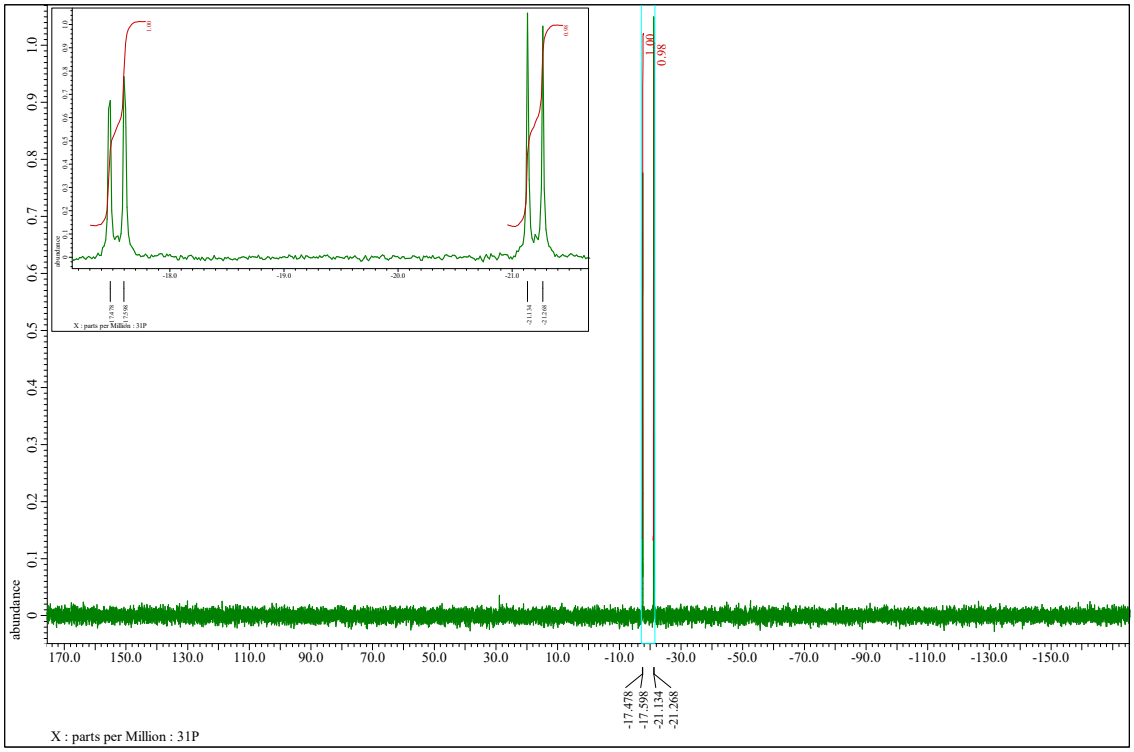


Fig. S9. ^{31}P NMR spectra of 3,5-xylyl-Benzoxantphos (**L5**) in $CDCl_3$.

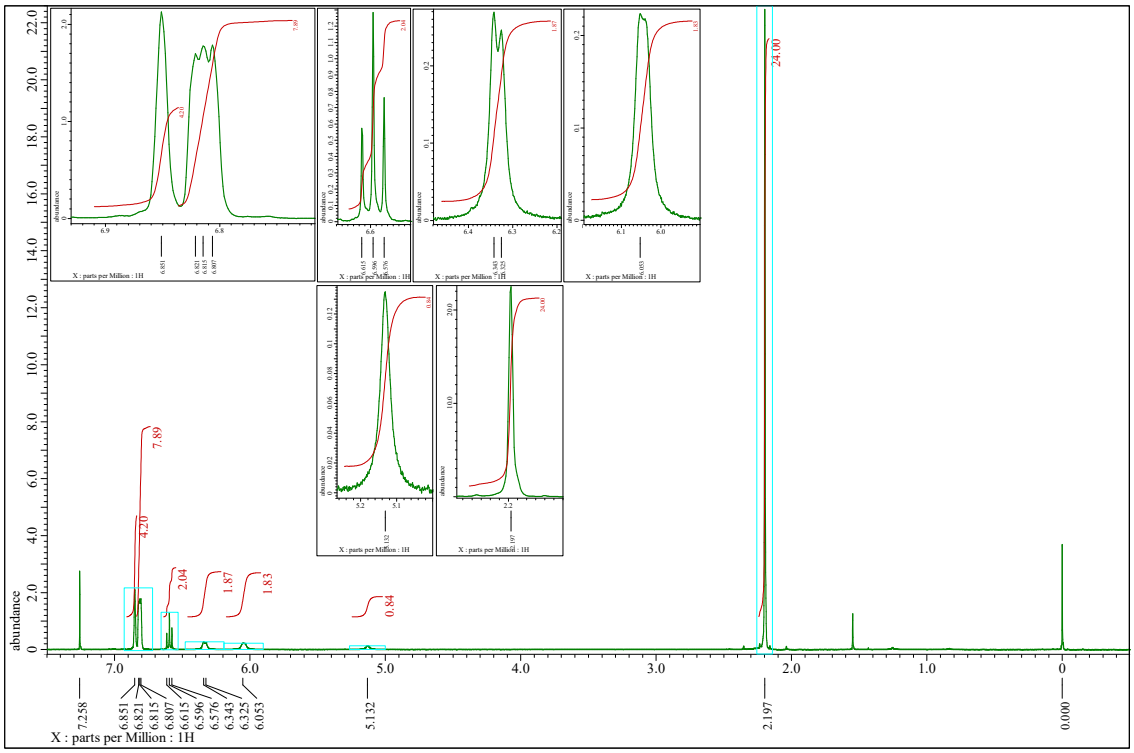


Fig. S10. ^{1}H NMR spectra of 3,5-xylyl-Nixantphos (**L6**) in $CDCl_3$.

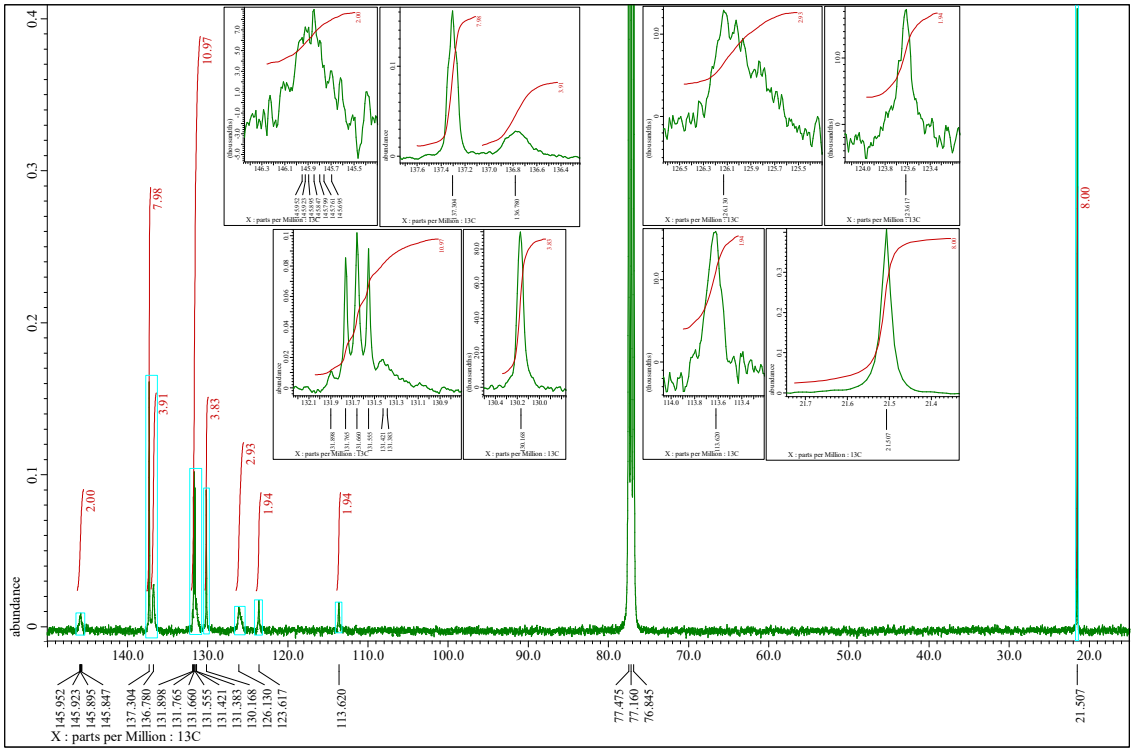


Fig. S11. ^{13}C NMR spectra of 3,5-xylyl-Nixantphos (**L6**) in $CDCl_3$ (inverse-gated proton decoupling).

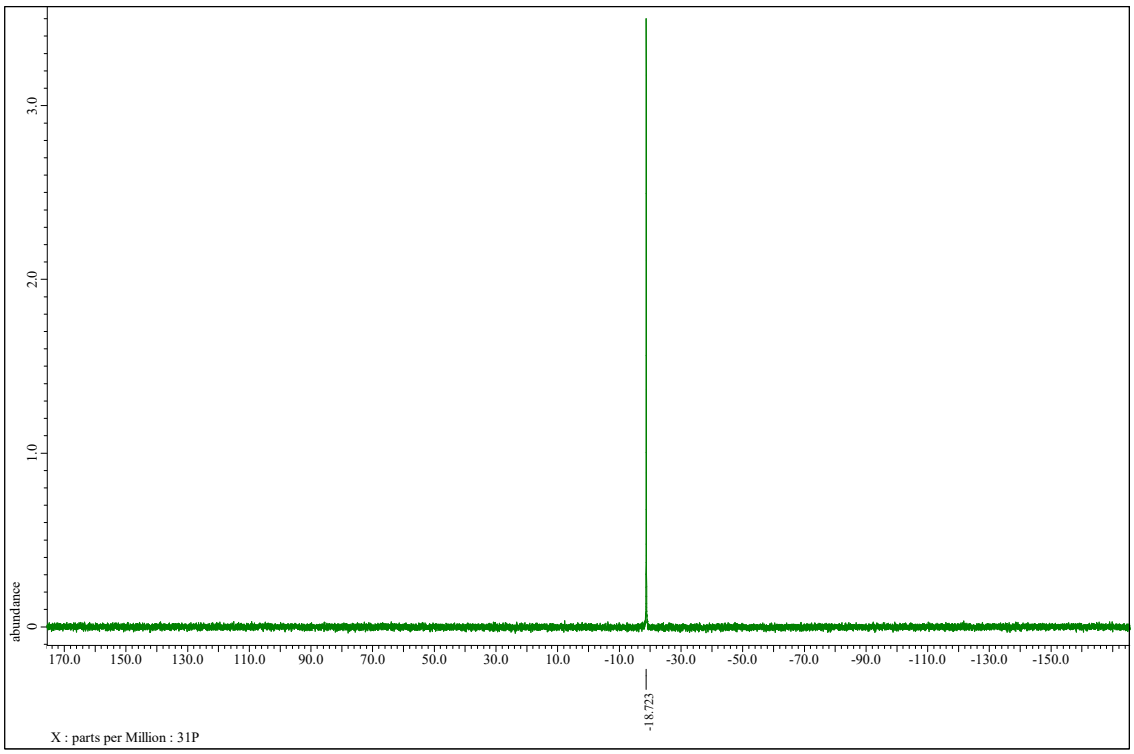


Fig. S12. ^{31}P NMR spectra of 3,5-xylyl-Nixantphos (**L6**) in $CDCl_3$.

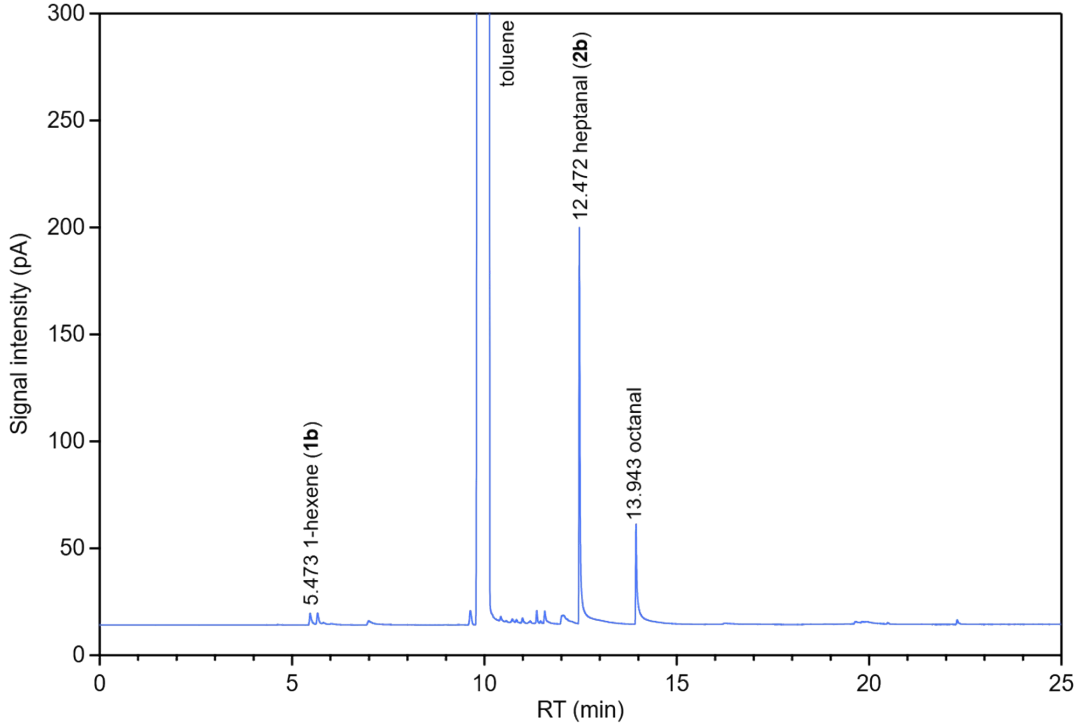


Fig. S13. GC-FID chromatogram of the hydroformylation of 1-hexene (**1b**).

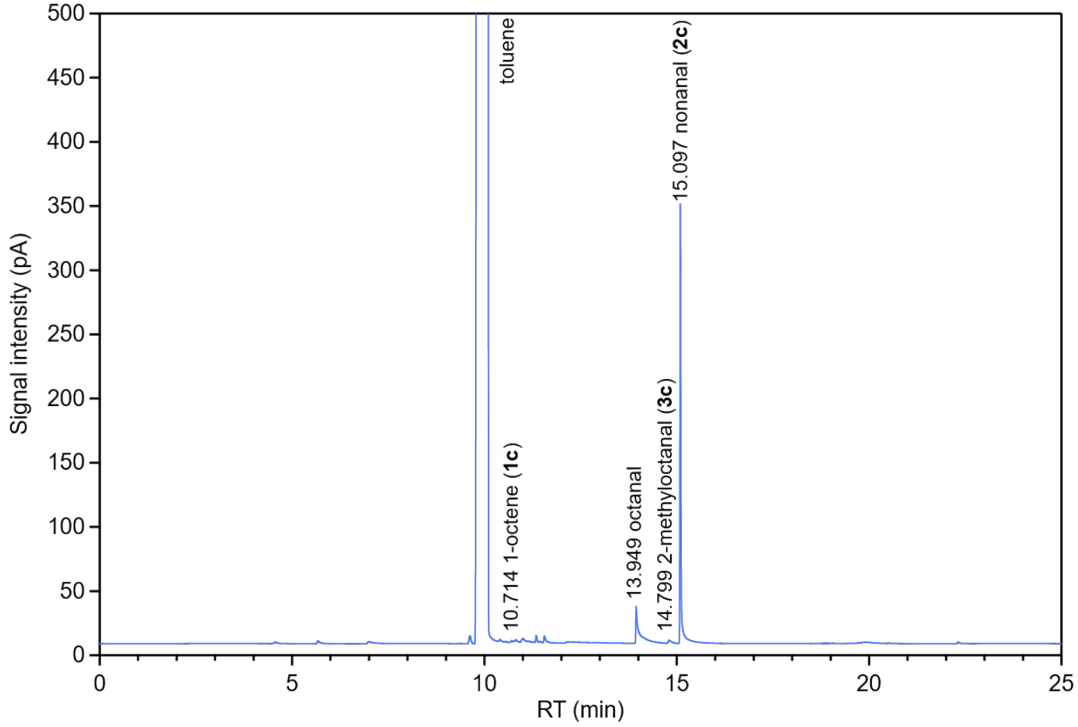


Fig. S14. GC-FID chromatogram of the hydroformylation of 1-octene (**1c**).

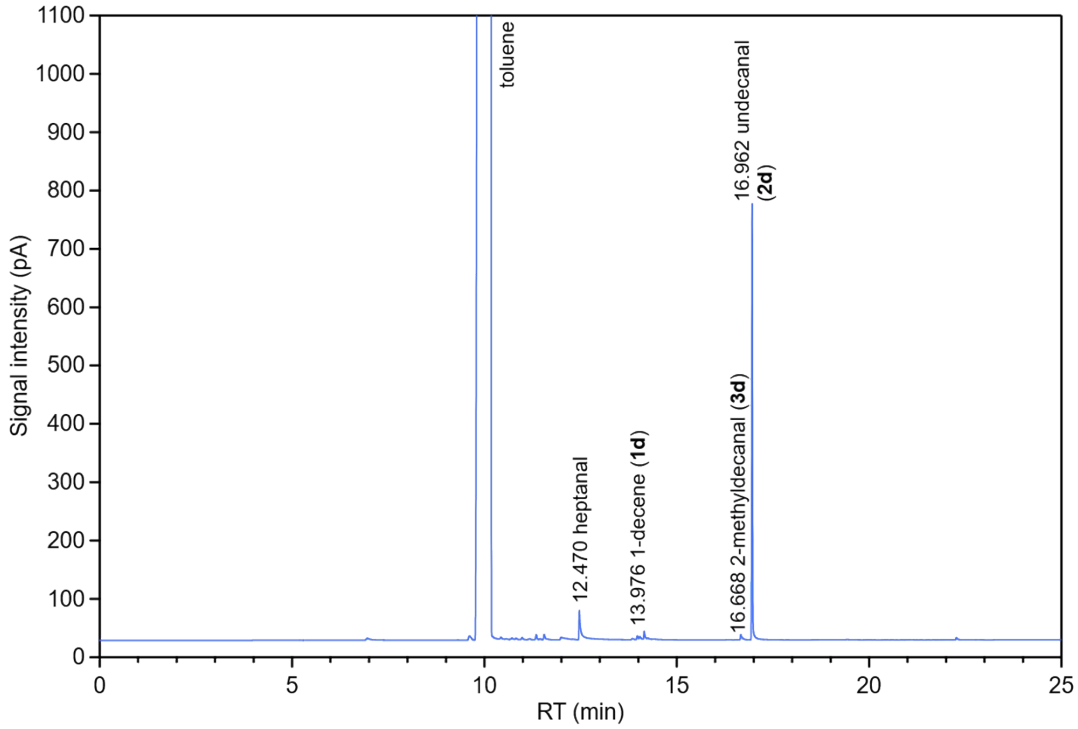


Fig. S15. GC-FID chromatogram of the hydroformylation of 1-decene (**1d**).

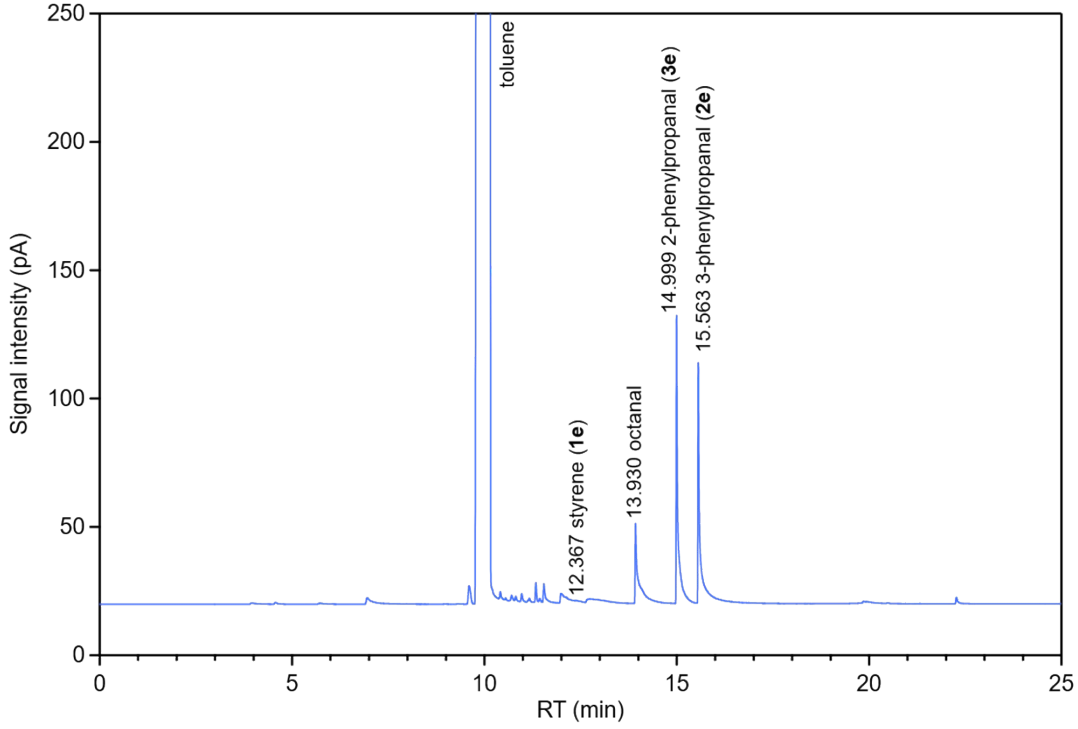


Fig. S16. GC-FID chromatogram of the hydroformylation of styrene (**1e**).

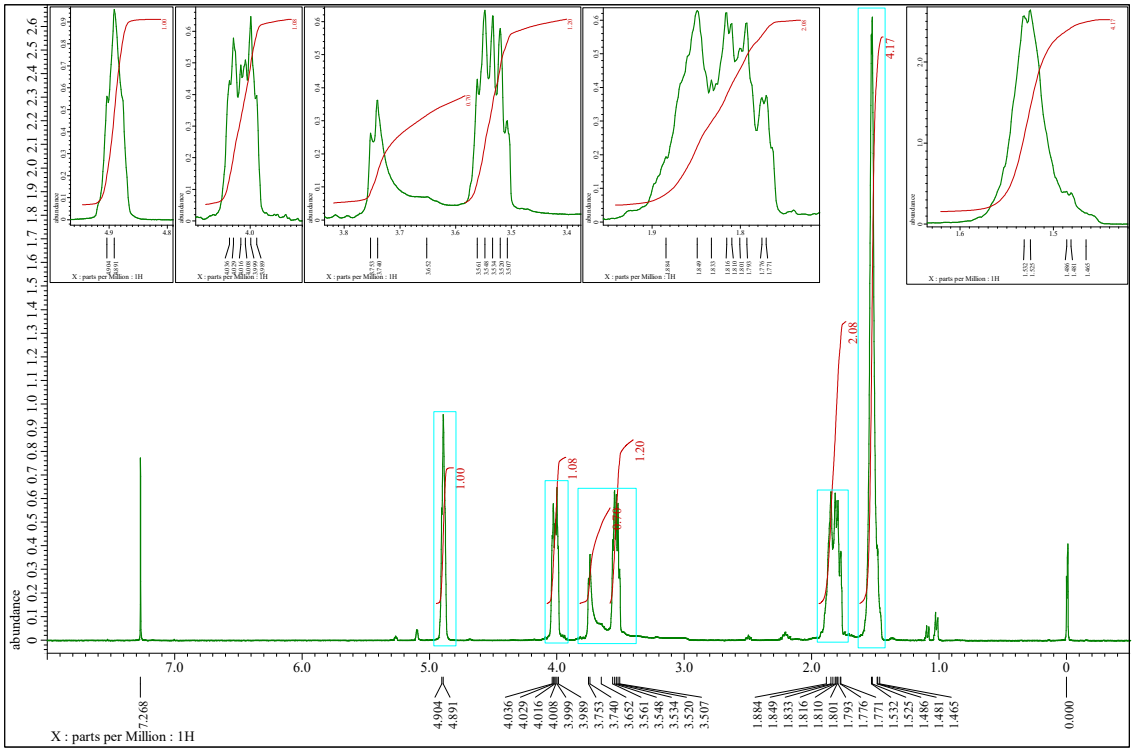


Fig. S17. ^{1}H NMR spectra of 2-hydroxytetrahydropyran (**2f**) in $CDCl_3$.

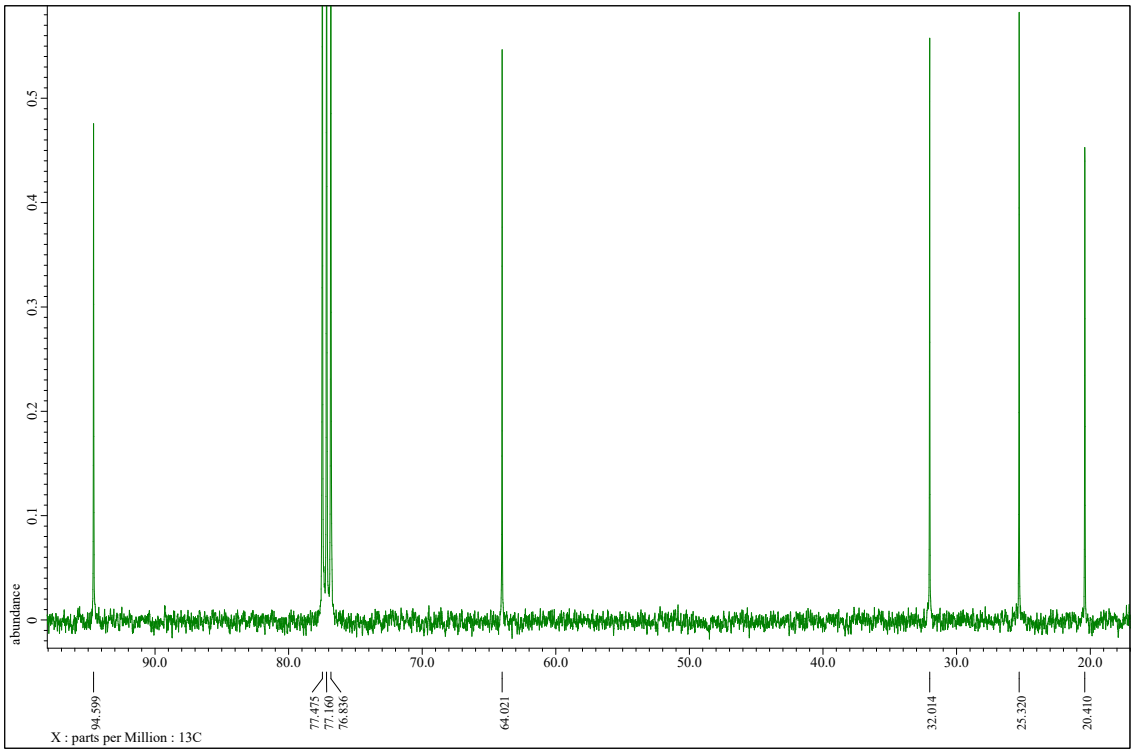


Fig. S18. ^{13}C NMR spectra of 2-hydroxytetrahydropyran (**2f**) in $CDCl_3$.

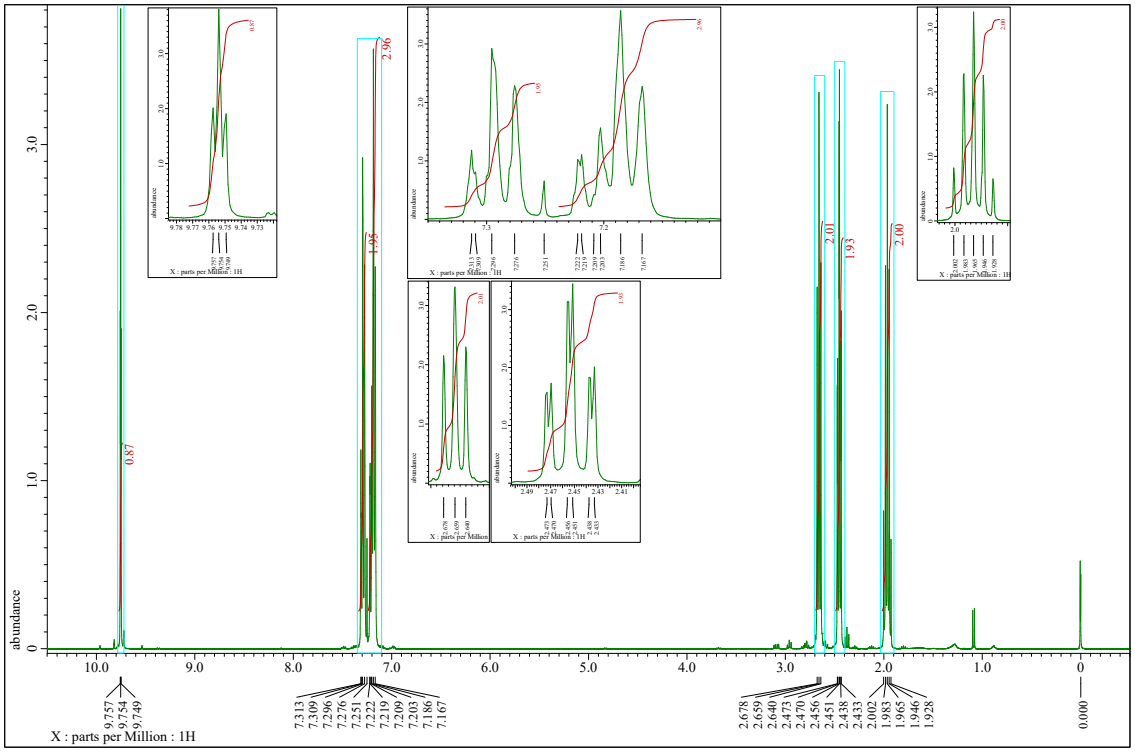


Fig. S19. ^{1}H NMR spectra of 4-phenylbutanal (**2g**) in $CDCl_3$.

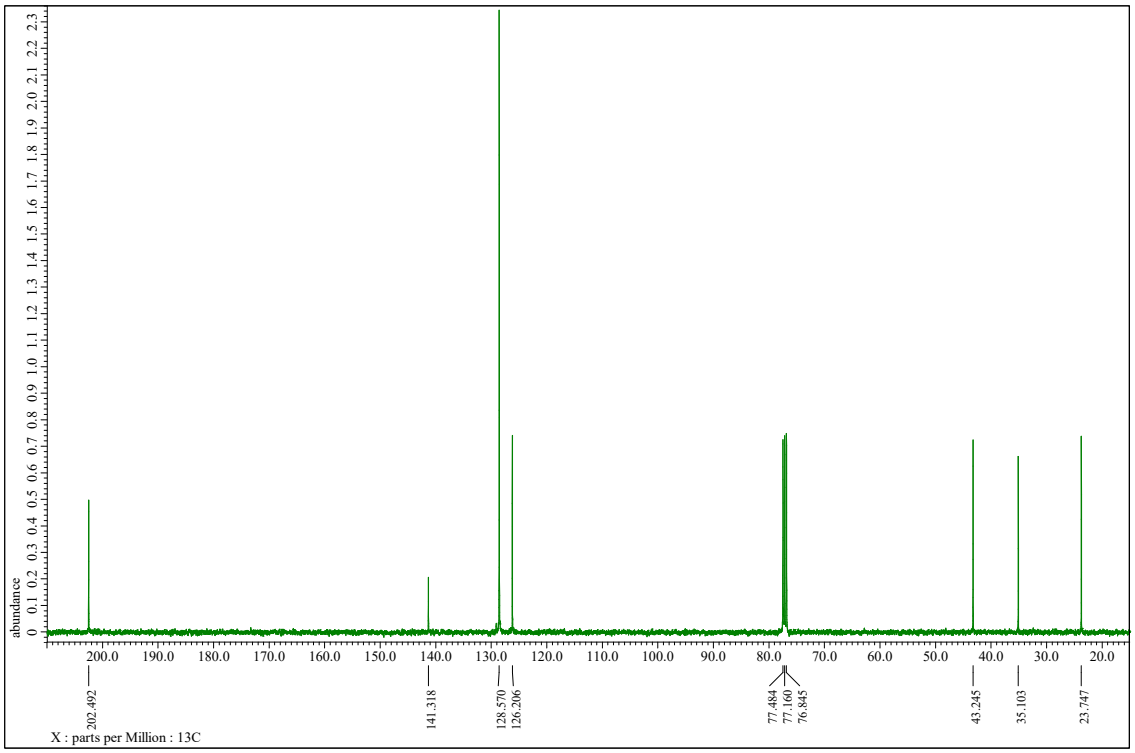


Fig. S20. ^{13}C NMR spectra of 4-phenylbutanal (**2g**) in $CDCl_3$.

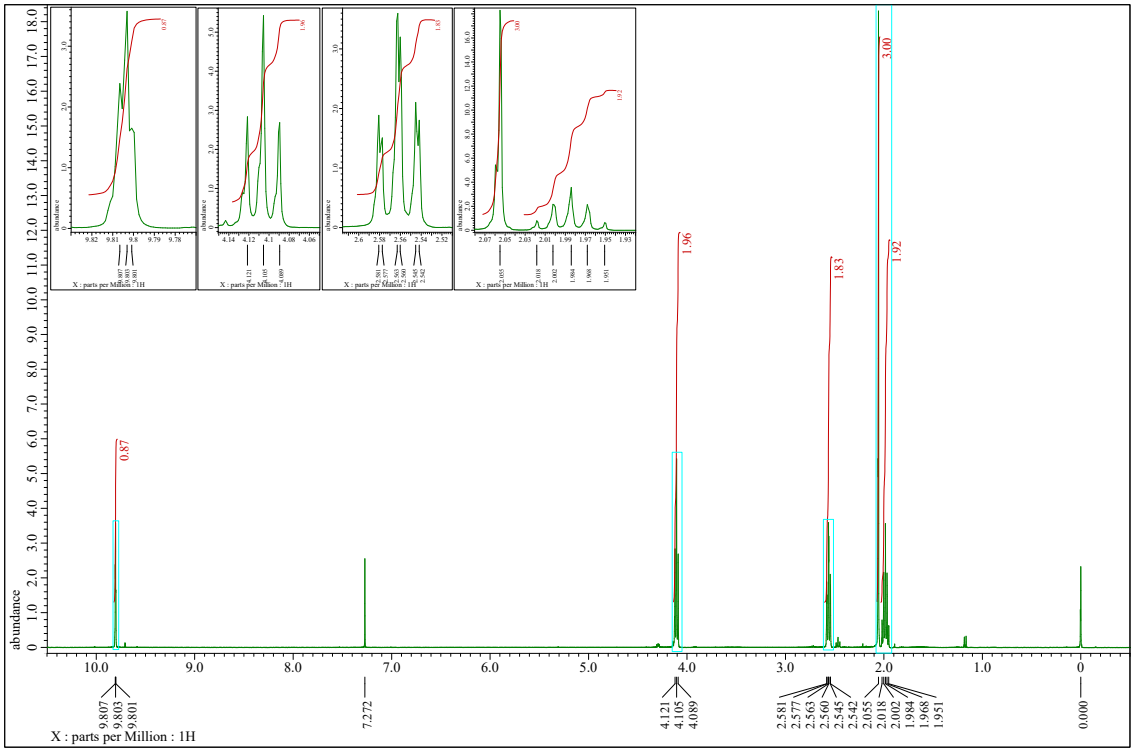


Fig. S21. ^{1}H NMR spectra of 4-acetoxybutanal (**2h**) in $CDCl_3$.

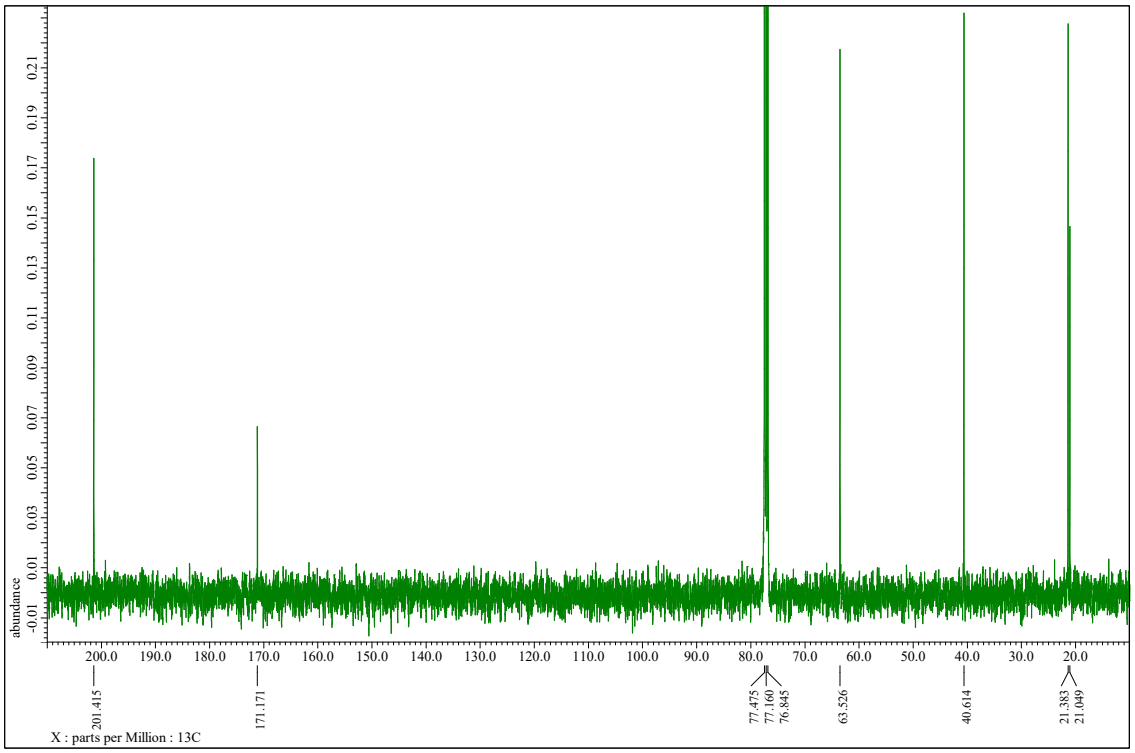


Fig. S22. ^{13}C NMR spectra of 4-acetoxybutanal (**2h**) in $CDCl_3$.

8. Computational details

To evaluate the origin of regioselectivity in the hydroformylation of **1a**, the activation free energy difference between the transition states (TSs) for 1,2- and 2,1-insertion was calculated. All DFT calculations were performed using Gaussian 16 programs.[6] Geometry optimizations and frequency analyses were performed employing the unrestricted ωB97XD functional in conjunction with the LANL2DZ basis set for Rh and the 6-31+G* basis set for the lighter atoms.

TS optimizations were conducted for both the 1,2- and 2,1-insertion processes. Frequency analyses were performed to confirm the nature of the stationary points (one imaginary frequency) and to obtain Gibbs free energies for the corresponding TSs. The activation free energy difference ($\Delta\Delta G‡$) was defined as the Gibbs free energy of the 2,1-insertion TS minus that of the 1,2-insertion TS.

TS optimizations (or geometry optimizations) were first carried out in the gas phase. Subsequently, frequency analyses were performed for the optimized structures using the polarizable continuum model (PCM) with toluene as the solvent to obtain the Gibbs free energies and activation barriers. This strategy provided a reasonable balance between computational efficiency and accuracy.

In some cases, depending on the nature of the aryl groups and the positions of their substituents on the bidentate phosphine ligands, self-consistent field (SCF) convergence was difficult to achieve within a practical time frame. When convergence within the default four thresholds of Gaussian 16 could not be reached, the integration accuracy was increased using int (grid = Ultrafine) option, which enabled reliable convergence of the molecular structures and Gibbs free energies required for the activation barrier calculations.

9. Cartesian coordinates and energies

Cartesian coordinates and total electronic and thermal free energies (in Hartree) of all optimized structures, including transition states, are given below.

L1

1,2-insertion

E (UwB97XD) = −2679.38939689

Zero-point correction = 0.708995 (Hartree/Particle)

Thermal correction to Energy = 0.753683

Thermal correction to Enthalpy = 0.754627

Thermal correction to Gibbs Free Energy = 0.629283

Sum of electronic and zero-point Energies = −2678.680402

Sum of electronic and thermal Energies = −2678.635714

Sum of electronic and thermal Enthalpies = −2678.634770

Sum of electronic and thermal Free Energies = −2678.760113

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.180981	-1.309625	-1.073340
1	-0.557272	-2.391810	-2.026173
6	0.357499	-0.204082	-2.597864
8	0.455400	0.470666	-3.530502
6	0.501772	-3.137948	0.102175
6	0.269397	-3.586041	-1.223752
15	1.845123	-0.122192	0.126489
15	-1.906930	-0.525973	-0.000145
1	1.532833	-3.125771	0.455662
1	-0.244863	-3.333330	0.868381
1	-0.653294	-4.142547	-1.397831
6	1.412000	-4.046446	-2.101647
1	1.197197	-3.864354	-3.156357
1	2.326336	-3.500679	-1.836215
8	1.606457	-5.452438	-1.990785
1	1.826206	-5.651961	-1.071693
6	-2.364516	1.185162	-0.526869
6	-3.583927	1.518632	-1.125352
6	-1.396222	2.190864	-0.467912
6	-3.795175	2.791152	-1.648556
1	-4.368315	0.773627	-1.206895
6	-1.573239	3.477035	-0.977893
6	-2.797075	3.760417	-1.582304
1	-4.744819	3.026659	-2.119866
1	-2.983191	4.741897	-2.006116
6	2.053990	1.602221	-0.467048
6	3.216292	2.137648	-1.022066
6	0.918972	2.412363	-0.438271
6	3.209496	3.427576	-1.549545
1	4.123040	1.541543	-1.060042

6	0.876684	3.706161	-0.949434	6	-3.464450	-1.431151	-0.406993
6	2.050122	4.200391	-1.520559	6	-4.605665	-1.385424	0.405477
1	4.114529	3.832145	-1.992723	6	-3.520901	-2.156240	-1.600644
1	2.070657	5.198481	-1.946307	6	-5.767734	-2.056810	0.035887
8	-0.203728	1.869822	0.132541	1	-4.588256	-0.819613	1.332797
6	3.546876	-0.801181	-0.054703	6	-4.686313	-2.823244	-1.976849
6	4.475158	-0.847787	0.989554	1	-2.644778	-2.192857	-2.242040
6	3.917438	-1.290787	-1.313337	6	-5.811152	-2.778426	-1.157318
6	5.749049	-1.375236	0.777794	1	-6.642279	-2.013134	0.679338
1	4.207765	-0.477498	1.974854	1	-4.710484	-3.381094	-2.908850
6	5.193269	-1.803244	-1.528809	6	-2.032913	-0.458896	1.835563
1	3.191948	-1.271954	-2.123593	6	-2.158218	-1.674708	2.523239
6	6.111922	-1.850525	-0.480181	6	-1.955000	0.721782	2.577653
1	6.457777	-1.413169	1.600511	6	-2.234821	-1.705686	3.911446
1	5.465597	-2.176110	-2.512249	1	-2.229991	-2.605912	1.965791
6	1.717526	0.126305	1.944350	6	-2.015753	0.690235	3.970166
6	1.225981	-0.915505	2.734927	1	-1.852581	1.678675	2.076668
6	2.146837	1.302363	2.568411	6	-2.163533	-0.519578	4.641609
6	1.187780	-0.797347	4.120908	1	-2.351163	-2.657494	4.423133
1	0.855110	-1.818871	2.264478	1	-1.948584	1.619510	4.529080
6	2.091201	1.429061	3.954832	1	7.104419	-2.261518	-0.642730
1	2.532393	2.125615	1.973490	1	1.577252	0.473104	5.816404
6	1.618819	0.375957	4.734954	1	-2.217896	-0.540530	5.726587
1	0.797485	-1.615732	4.718109	1	-6.718098	-3.303156	-1.444763
1	2.423987	2.350908	4.424296	6	-0.432055	4.478028	-0.787754

6	-0.497842	5.021492	0.661425
1	0.327098	5.720897	0.839648
1	-1.446310	5.545944	0.824458
1	-0.422951	4.210684	1.393437
6	-0.529107	5.654361	-1.763033
1	-1.460040	6.208902	-1.609312
1	0.286200	6.364597	-1.593235
1	-0.489537	5.319599	-2.805087

2,1-insertion

E (UwB97XD) = −2679.38100127

Zero-point correction = 0.708463 (Hartree/Particle)

Thermal correction to Energy = 0.753390

Thermal correction to Enthalpy = 0.754334

Thermal correction to Gibbs Free Energy = 0.628525

Sum of electronic and zero-point Energies = −2678.672538

Sum of electronic and thermal Energies = −2678.627612

Sum of electronic and thermal Enthalpies = −2678.626667

Sum of electronic and thermal Free Energies = −2678.752476

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.254858	-1.485093	-0.833848
1	-0.559018	-2.884437	-0.835147
6	0.245425	-1.008173	-2.725633
8	0.215826	-0.733160	-3.846690
6	1.740958	-3.031137	-0.698131
6	0.591955	-3.571606	-0.024355
15	1.773920	0.133142	0.141644
15	-1.828080	-0.681789	-0.002037
1	2.559869	-2.688141	-0.067902
1	0.536770	-3.536419	1.061079
1	0.136708	-4.478404	-0.432154
6	2.195374	-3.660345	-1.991126
1	2.779083	-2.953600	-2.583945
1	1.320144	-3.960864	-2.587099
8	3.065234	-4.772364	-1.782794
1	2.632859	-5.380856	-1.170469
6	-2.525000	0.921499	-0.590388
6	-1.701489	2.043899	-0.548766
6	-3.774888	1.072798	-1.198764
6	-2.034560	3.282794	-1.093948
6	-4.146219	2.295980	-1.750739

1	-4.453824	0.229355	-1.265692	6	1.368996	-0.626935	2.776952
6	-3.281716	3.388499	-1.707780	6	1.950150	1.697392	2.529123
1	-5.115697	2.395574	-2.229744	6	1.343117	-0.477247	4.160000
1	-3.591343	4.326040	-2.158422	1	1.129819	-1.587748	2.328365
8	-0.489465	1.883889	0.070209	6	1.904396	1.854070	3.913044
6	0.561278	2.528823	-0.529811	1	2.199071	2.548843	1.901499
6	1.773901	1.845208	-0.541169	6	1.607317	0.765768	4.731182
6	0.368462	3.795278	-1.076422	1	1.094149	-1.326327	4.789489
6	2.868246	2.499887	-1.111117	1	2.107623	2.827294	4.351836
6	1.476967	4.404446	-1.664315	6	-3.249546	-1.795215	-0.384218
6	2.715996	3.766082	-1.672443	6	-4.369569	-1.890253	0.450670
1	3.839760	2.017023	-1.130936	6	-3.244438	-2.506942	-1.588162
1	1.385312	5.387018	-2.116152	6	-5.452556	-2.690970	0.095706
1	3.571799	4.258803	-2.124267	1	-4.400234	-1.335370	1.384084
6	3.547861	-0.303686	-0.085832	6	-4.332021	-3.300342	-1.949127
6	4.477063	-0.337503	0.955962	1	-2.382242	-2.438590	-2.245312
6	3.968151	-0.643204	-1.378924	6	-5.436765	-3.397944	-1.105939
6	5.800199	-0.708077	0.709763	1	-6.311011	-2.758990	0.758287
1	4.174584	-0.079652	1.966551	1	-4.311714	-3.845007	-2.888935
6	5.287769	-1.002672	-1.626460	6	-1.945801	-0.577700	1.831472
1	3.248114	-0.631921	-2.193652	6	-1.846912	-1.779051	2.546574
6	6.208644	-1.039784	-0.578597	6	-2.083507	0.616561	2.539077
1	6.510141	-0.737785	1.531797	6	-1.918514	-1.788397	3.934279
1	5.594620	-1.268405	-2.634048	1	-1.729786	-2.716931	2.008049
6	1.683708	0.453752	1.949225	6	-2.129652	0.610377	3.933540

1	-2.159461	1.562059	2.012060
6	-2.057237	-0.589113	4.633941
1	-1.858694	-2.731399	4.471266
1	-2.225627	1.550330	4.469741
1	1.573762	0.887927	5.810404
1	-2.101238	-0.591603	5.719551
1	-6.282112	-4.021748	-1.383041
1	7.237362	-1.333407	-0.767282
6	-1.021146	4.416480	-0.933059
6	-1.152160	4.989230	0.500223
1	-0.414078	5.784170	0.656863
1	-2.155140	5.405005	0.650066
1	-0.984496	4.213784	1.254790
6	-1.254855	5.544268	-1.941758
1	-2.245728	5.988029	-1.802970
1	-0.529732	6.350676	-1.793977
1	-1.173635	5.186878	-2.973870

L2

1,2-insertion

E (UwB97XD) = −2616.80828682

Zero-point correction = 0.640750 (Hartree/Particle)

Thermal correction to Energy = 0.682585

Thermal correction to Enthalpy = 0.683529

Thermal correction to Gibbs Free Energy = 0.564176

Sum of electronic and zero-point Energies = −2616.167537

Sum of electronic and thermal Energies = −2616.125702

Sum of electronic and thermal Enthalpies = −2616.124758

Sum of electronic and thermal Free Energies = −2616.244110

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.107154	-1.181900	-0.950440
1	-0.681854	-2.324265	-1.784728
6	0.325436	-0.250452	-2.581215
8	0.448467	0.317581	-3.579950
6	0.336292	-2.889450	0.411401
6	0.088510	-3.464257	-0.862389
15	1.842000	0.037134	0.118279
15	-1.959960	-0.202865	0.017234
1	1.365185	-2.889688	0.771452
1	-0.421702	-2.969289	1.187279
1	-0.856767	-3.996023	-0.985002

6	1.213910	-4.060553	-1.678742	1	-0.257137	5.157065	-2.156836
1	1.010049	-3.981019	-2.748256	6	3.508699	-0.733982	-0.002769
1	2.149116	-3.527332	-1.465200	6	4.436194	-0.735864	1.043079
8	1.349583	-5.453981	-1.420407	6	3.851506	-1.346755	-1.214565
1	1.560389	-5.565102	-0.484443	6	5.683008	-1.339647	0.878739
6	-2.329764	1.461862	-0.697602	1	4.189308	-0.270465	1.992753
6	-3.534480	1.813538	-1.324556	6	5.100887	-1.935855	-1.383676
6	-1.295795	2.389178	-0.750307	1	3.125374	-1.363938	-2.024242
6	-3.656278	3.030381	-1.988942	6	6.019297	-1.937012	-0.333662
1	-4.374565	1.127788	-1.308408	1	6.391337	-1.341112	1.702669
6	-1.381067	3.593446	-1.451635	1	5.352386	-2.404161	-2.331188
6	-2.581898	3.916595	-2.073783	1	6.990735	-2.407009	-0.459478
1	-4.595709	3.285945	-2.469876	6	1.737410	0.476913	1.899704
1	-2.677077	4.849955	-2.623094	6	1.166230	-0.436263	2.789465
6	2.123035	1.679728	-0.656315	6	2.255163	1.676061	2.400591
6	3.308718	2.127792	-1.249333	6	1.136092	-0.170692	4.155237
6	1.010729	2.505862	-0.727968	1	0.726621	-1.352374	2.412127
6	3.332618	3.350457	-1.916741	6	2.209130	1.950703	3.765571
1	4.204952	1.517427	-1.200028	1	2.698954	2.401869	1.724755
6	0.999984	3.709293	-1.430666	6	1.656364	1.023891	4.646951
6	2.183116	4.134737	-2.028300	1	0.683306	-0.889589	4.831144
1	4.254454	3.691968	-2.377800	1	2.609760	2.889144	4.139157
1	2.207257	5.071021	-2.580290	1	1.621559	1.236801	5.711931
8	-0.131459	2.119327	-0.067498	6	-3.555100	-1.070302	-0.316038
7	-0.224940	4.397516	-1.490288	6	-4.698171	-0.893862	0.475423

6	-3.636622	-1.904378	-1.434807
6	-5.887534	-1.544528	0.158919
1	-4.660693	-0.242483	1.344119
6	-4.828925	-2.550998	-1.758112
1	-2.758561	-2.043174	-2.059422
6	-5.956030	-2.375709	-0.959427
1	-6.763587	-1.399054	0.785131
1	-4.872552	-3.194983	-2.632046
1	-6.884340	-2.884097	-1.205036
6	-2.089387	0.061925	1.833742
6	-2.275618	-1.067184	2.644533
6	-1.948649	1.308899	2.446996
6	-2.349506	-0.947892	4.028180
1	-2.396339	-2.047069	2.187926
6	-2.008487	1.426927	3.834920
1	-1.793979	2.200598	1.848744
6	-2.216202	0.303546	4.629404
1	-2.512821	-1.833345	4.636975
1	-1.891842	2.405157	4.292921
1	-2.268809	0.399678	5.710423

2,1-insertion

E (UwB97XD) = −2616.79969161

Zero-point correction = 0.639882 (Hartree/Particle)

Thermal correction to Energy = 0.682023

Thermal correction to Enthalpy = 0.682967

Thermal correction to Gibbs Free Energy = 0.562606

Sum of electronic and zero-point Energies = −2616.159810

Sum of electronic and thermal Energies = −2616.117668

Sum of electronic and thermal Enthalpies = −2616.116724

Sum of electronic and thermal Free Energies = −2616.237086

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.064887	-1.368494	-0.642771
1	-0.894079	-2.658931	-0.453907
6	0.113539	-1.171347	-2.582933
8	0.117183	-1.057893	-3.732188
6	1.375461	-3.024383	-0.251829
6	0.170561	-3.337212	0.467701
15	1.764782	0.196774	0.108674
15	-1.937330	-0.246854	0.020494
1	2.222240	-2.682031	0.340920
1	0.113111	-3.138380	1.535259

1	-0.375545	-4.241683	0.185546	7	-0.543744	4.307351	-1.835179
6	1.769741	-3.878448	-1.430539	1	-0.620248	5.017328	-2.550911
1	2.429596	-3.328774	-2.104383	6	3.477721	-0.459382	-0.039486
1	0.872114	-4.169727	-1.997099	6	4.395731	-0.469653	1.012585
8	2.515296	-5.032632	-1.045207	6	3.855955	-1.003928	-1.274159
1	2.015288	-5.499225	-0.363722	6	5.667198	-1.017461	0.834100
6	-2.449549	1.313834	-0.820782	1	4.124118	-0.054717	1.978719
6	-1.487025	2.302912	-0.943038	6	5.125452	-1.540207	-1.455188
6	-3.679089	1.531111	-1.459453	1	3.142959	-1.011877	-2.095136
6	-1.650023	3.443681	-1.730552	6	6.035176	-1.551783	-0.397057
6	-3.884807	2.688114	-2.205636	1	6.368369	-1.025936	1.664088
1	-4.468967	0.791371	-1.389164	1	5.400453	-1.962725	-2.417427
6	-2.873056	3.637313	-2.363684	1	7.023110	-1.982681	-0.532550
1	-4.840778	2.845066	-2.696048	6	1.718536	0.785973	1.847576
1	-3.034893	4.518735	-2.979190	6	1.247581	-0.105368	2.814773
8	-0.315021	2.154494	-0.242516	6	2.162187	2.050195	2.246214
6	0.797494	2.542208	-0.949786	6	1.241174	0.248034	4.160685
6	1.944873	1.776864	-0.825602	1	0.870139	-1.076152	2.503843
6	0.717670	3.690032	-1.737978	6	2.137869	2.412705	3.591283
6	3.103655	2.247724	-1.457421	1	2.530121	2.756198	1.506559
6	1.872892	4.132058	-2.374903	6	1.683614	1.510032	4.551291
6	3.061554	3.417666	-2.212055	1	0.869358	-0.454390	4.900596
1	4.034316	1.697928	-1.366557	1	2.478669	3.400630	3.889101
1	1.847021	5.026382	-2.992534	1	1.666474	1.792934	5.600329
1	3.964694	3.772771	-2.699255	6	-3.465094	-1.248679	-0.235794

6	-4.595008	-1.110805	0.579343
6	-3.525424	-2.116549	-1.330946
6	-5.753567	-1.836840	0.313045
1	-4.573502	-0.432449	1.427582
6	-4.687739	-2.835368	-1.604184
1	-2.656051	-2.229546	-1.972245
6	-5.803007	-2.700803	-0.780132
1	-6.619475	-1.723781	0.959581
1	-4.717811	-3.503727	-2.460136
1	-6.707258	-3.266174	-0.988041
6	-2.055324	0.138317	1.814810
6	-2.091230	-0.947425	2.700586
6	-2.058840	1.432641	2.335039
6	-2.162223	-0.742277	4.073131
1	-2.079186	-1.962180	2.308617
6	-2.105977	1.638574	3.714214
1	-2.024481	2.291615	1.672933
6	-2.167132	0.555869	4.585187
1	-2.207160	-1.595653	4.744647
1	-2.096260	2.652607	4.103754
1	-2.210734	0.719760	5.658392

L3

1,2-insertion

E (UwB97XD) = −2715.07055340

Zero-point correction = 0.670611 (Hartree/Particle)

Thermal correction to Energy = 0.714153

Thermal correction to Enthalpy = 0.715098

Thermal correction to Gibbs Free Energy = 0.591528

Sum of electronic and zero-point Energies = −2714.399942

Sum of electronic and thermal Energies = −2714.356400

Sum of electronic and thermal Enthalpies = −2714.355456

Sum of electronic and thermal Free Energies = −2714.479025

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.531043	-1.059400	-1.213301
1	0.021146	-2.148764	-2.296379
6	0.291145	0.263237	-2.540385
8	0.140068	1.073961	-3.350274
6	1.404318	-2.885874	-0.362192
6	1.197391	-3.176082	-1.735532
15	1.923440	0.347405	0.117361
15	-1.643428	-1.058378	0.039703

1	2.420264	-2.649631	-0.045459	8	-0.557890	1.622518	0.317749
1	0.794606	-3.387718	0.385734	6	3.724768	0.186801	-0.220245
1	0.444194	-3.930321	-1.970120	6	4.704114	0.213180	0.776931
6	2.350757	-3.166645	-2.714546	6	4.118774	0.034410	-1.555519
1	2.014820	-2.893676	-3.716697	6	6.052985	0.089103	0.443242
1	3.104095	-2.436222	-2.392350	1	4.418866	0.325888	1.818846
8	2.920657	-4.464666	-2.845066	6	5.465243	-0.074421	-1.889735
1	3.253100	-4.733377	-1.978978	1	3.358116	-0.005993	-2.332069
6	-2.578480	0.528355	-0.103087	6	6.436350	-0.051378	-0.888438
6	-3.972745	0.646220	-0.351318	1	6.803783	0.102771	1.228529
6	-1.859371	1.702829	-0.064884	1	5.755005	-0.189291	-2.930442
6	-4.570123	1.867610	-0.549099	6	1.856932	0.262785	1.953660
1	-4.579950	-0.252927	-0.386622	6	1.705594	-0.985237	2.564362
6	-2.406398	2.972633	-0.354730	6	2.006564	1.395306	2.760968
6	-3.803465	3.064674	-0.568054	6	1.734487	-1.104952	3.950190
1	-5.642397	1.926709	-0.715454	1	1.548103	-1.867204	1.954538
6	1.649330	2.144687	-0.174281	6	2.014790	1.278856	4.149628
6	2.608882	3.085088	-0.541407	1	2.121963	2.376305	2.308818
6	0.322524	2.571541	-0.100414	6	1.888149	0.026941	4.747131
6	2.226964	4.395547	-0.841464	1	1.611583	-2.082551	4.406069
1	3.653018	2.794590	-0.612380	1	2.126274	2.168880	4.762992
6	-0.104078	3.858664	-0.429884	6	-2.931202	-2.249874	-0.532249
6	0.889084	4.772488	-0.803065	6	-3.932494	-2.767995	0.299374
1	2.980529	5.120021	-1.134754	6	-2.928354	-2.611393	-1.883572
1	0.613023	5.783281	-1.087768	6	-4.898238	-3.634242	-0.207637

1	-3.962357	-2.493519	1.350054
6	-3.900187	-3.469628	-2.394784
1	-2.157935	-2.214549	-2.539185
6	-4.885075	-3.987193	-1.556630
1	-5.665091	-4.030200	0.452673
1	-3.881992	-3.737473	-3.447530
6	-1.635087	-1.367917	1.852904
6	-1.375931	-2.669013	2.306785
6	-1.800278	-0.351063	2.796588
6	-1.319254	-2.951010	3.667786
1	-1.249765	-3.476963	1.589527
6	-1.728432	-0.630209	4.160364
1	-1.993677	0.667147	2.473031
6	-1.497422	-1.929981	4.601116
1	-1.137394	-3.969973	3.999423
1	-1.855491	0.174994	4.878545
1	7.487323	-0.148496	-1.146113
1	1.897909	-0.064920	5.829784
1	-1.449723	-2.146743	5.664758
1	-5.638579	-4.663242	-1.951177
6	-1.557158	4.115701	-0.454844
6	-2.139299	5.346846	-0.670937
1	-1.528817	6.241725	-0.744118
6	-3.539805	5.459940	-0.824786
1	-3.972050	6.442308	-0.992584
6	-4.354074	4.352503	-0.795756
1	-5.425450	4.451180	-0.949141

2,1-insertion

E (UwB97XD) = −2715.06202721

Zero-point correction = 0.668370 (Hartree/Particle)

Thermal correction to Energy = 0.711448

Thermal correction to Enthalpy = 0.712392

Thermal correction to Gibbs Free Energy = 0.590794

Sum of electronic and zero-point Energies = −2714.393657

Sum of electronic and thermal Energies = −2714.350579

Sum of electronic and thermal Enthalpies = −2714.349635

Sum of electronic and thermal Free Energies = −2714.471234

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z

45	0.545192	-1.218053	-1.057701
1	0.028969	-2.728665	-1.320919
6	0.260612	-0.365959	-2.787708

8	0.076191	0.120261	-3.818997	6	2.374029	3.247154	-0.461123
6	2.310316	-2.398163	-1.347411	6	0.572012	4.839569	-0.771731
6	1.363439	-3.302832	-0.751156	6	1.929255	4.536765	-0.765123
15	1.827661	0.462370	0.174873	1	3.435334	3.021469	-0.495860
15	-1.596175	-1.088830	0.031515	1	0.249868	5.836295	-1.057839
1	3.104116	-2.028621	-0.700053	1	2.651691	5.304554	-1.024815
1	1.411877	-3.508023	0.315773	6	3.627251	0.453193	-0.207673
1	1.061917	-4.182175	-1.327249	6	4.627101	0.374511	0.763763
6	2.753640	-2.631479	-2.769875	6	3.996031	0.502943	-1.558822
1	3.123200	-1.706971	-3.217680	6	5.971843	0.341833	0.390332
1	1.902784	-2.983327	-3.372945	1	4.363227	0.334838	1.816574
8	3.844762	-3.546748	-2.860582	6	5.335133	0.479579	-1.930428
1	3.602963	-4.350125	-2.382838	1	3.222794	0.551169	-2.322028
6	-2.654626	0.409061	-0.145105	6	6.328583	0.394987	-0.953837
6	-2.012224	1.623169	-0.102947	1	6.739436	0.272867	1.156237
6	-4.047718	0.432119	-0.420871	1	5.603904	0.512322	-2.982384
6	-2.626731	2.854895	-0.412212	6	1.817794	0.390436	2.010583
6	-4.713844	1.614306	-0.640750	6	1.794237	-0.877321	2.598729
1	-4.595593	-0.504153	-0.462059	6	1.874557	1.519260	2.832709
6	-4.022036	2.857242	-0.654366	6	1.859052	-1.018330	3.981088
1	-5.783738	1.606403	-0.830611	1	1.711791	-1.756570	1.964602
8	-0.719433	1.610038	0.303530	6	1.915510	1.380021	4.218929
6	0.113030	2.605759	-0.099183	1	1.891021	2.512963	2.393571
6	1.458585	2.247254	-0.135060	6	1.916861	0.111349	4.794875
6	-0.378927	3.868776	-0.435778	1	1.840074	-2.009945	4.423106

1	1.952844	2.265222	4.848116
6	-2.787429	-2.378339	-0.531217
6	-3.748772	-2.943844	0.314738
6	-2.775614	-2.747089	-1.880791
6	-4.668731	-3.867956	-0.176288
1	-3.783035	-2.663814	1.363802
6	-3.702271	-3.662929	-2.374586
1	-2.032988	-2.316379	-2.546466
6	-4.648372	-4.229081	-1.522497
1	-5.404127	-4.302907	0.495025
1	-3.679873	-3.936860	-3.425625
6	-1.549148	-1.380400	1.845878
6	-1.154107	-2.647131	2.296442
6	-1.828883	-0.387219	2.785012
6	-1.082074	-2.925114	3.656343
1	-0.918616	-3.425826	1.574131
6	-1.731377	-0.658423	4.149901
1	-2.129202	0.604179	2.459339
6	-1.370072	-1.927948	4.589119
1	-0.794052	-3.918750	3.989497
1	-1.942033	0.128449	4.868625
1	1.952768	0.003243	5.875507
1	-1.303421	-2.139427	5.652773
1	-5.366530	-4.949063	-1.905060
1	7.375225	0.363578	-1.242954
6	-1.843291	4.044092	-0.500405
6	-2.493669	5.236387	-0.739582
1	-1.937859	6.166633	-0.806557
6	-3.894972	5.261797	-0.925665
1	-4.381636	6.215012	-1.111793
6	-4.643354	4.108205	-0.904562
1	-5.714966	4.142660	-1.081969

L4

1,2-insertion

E (UwB97XD) = −2887.08399616

Zero-point correction = 0.750869 (Hartree/Particle)

Thermal correction to Energy = 0.798754

Thermal correction to Enthalpy = 0.799699

Thermal correction to Gibbs Free Energy = 0.665085

Sum of electronic and zero-point Energies = −2886.333127

Sum of electronic and thermal Energies = −2886.285242

Sum of electronic and thermal Enthalpies = −2886.284298

Sum of electronic and thermal Free Energies = −2886.418911

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	-1.896210	0.551474	-1.009914
1	-2.543488	1.719875	-1.926278
6	-1.072087	-0.115665	-2.576351
8	-0.566207	-0.513628	-3.535747
6	-3.600499	1.136083	0.244920
6	-3.951028	1.539854	-1.070164
15	-1.612173	-1.493926	0.155812
15	-0.159505	2.014230	-0.022415
1	-4.057595	0.224675	0.630398
1	-3.388041	1.894923	0.994515
1	-4.024701	2.614065	-1.249279
6	-4.928669	0.734812	-1.897311
1	-4.715821	0.832011	-2.963635
1	-4.857555	-0.326351	-1.626710
8	-6.258027	1.216692	-1.729913
1	-6.495541	1.120009	-0.798764
6	1.531305	1.578077	-0.626034
6	2.406170	2.474559	-1.257877
6	1.926807	0.247672	-0.567356
6	3.596255	2.021877	-1.815160
1	2.150125	3.526253	-1.325375
6	3.100499	-0.238080	-1.151061
6	3.945798	0.671129	-1.782249
1	4.263910	2.728669	-2.298676
1	4.875489	0.343386	-2.233265
6	-0.217747	-2.490708	-0.504823
6	-0.307879	-3.769637	-1.066416
6	1.021337	-1.868540	-0.505939
6	0.816954	-4.351397	-1.641270
1	-1.255745	-4.298357	-1.067435
6	2.161357	-2.419924	-1.096576
6	2.041756	-3.680419	-1.682204
1	0.741259	-5.337492	-2.089673
1	2.885446	-4.144133	-2.181971
8	1.137997	-0.649288	0.117592
7	3.324895	-1.628569	-1.058648
6	-3.028105	-2.660310	0.002483
6	-3.514276	-3.429146	1.063718
6	-3.645988	-2.766335	-1.250122
6	-4.597551	-4.287803	0.874637
1	-3.053893	-3.358602	2.044730
6	-4.715936	-3.634686	-1.442968
1	-3.285172	-2.154117	-2.073575
6	-5.197529	-4.395651	-0.377451
1	-4.970572	-4.873073	1.710632
1	-5.181503	-3.707525	-2.421872

6	-1.267288	-1.525528	1.960873
6	-1.851837	-0.556811	2.779772
6	-0.473783	-2.517828	2.546818
6	-1.668773	-0.590653	4.159259
1	-2.437992	0.239590	2.335902
6	-0.276098	-2.542611	3.925348
1	-0.007321	-3.278345	1.926494
6	-0.879378	-1.582437	4.735578
1	-2.125866	0.174335	4.779322
1	0.347009	-3.316346	4.365746
6	-0.214407	3.809934	-0.448433
6	0.409786	4.795202	0.328589
6	-0.868476	4.196404	-1.621736
6	0.370336	6.132671	-0.055757
1	0.933207	4.516960	1.239005
6	-0.902691	5.534415	-2.012727
1	-1.350346	3.440272	-2.235277
6	-0.286763	6.506198	-1.228258
1	0.857273	6.884037	0.559981
1	-1.415574	5.814905	-2.928506
6	0.043554	2.109292	1.804694
6	-0.938818	2.797438	2.531599
6	1.079894	1.488209	2.505170
6	-0.871379	2.884889	3.917818
1	-1.749533	3.296790	2.005640
6	1.139933	1.562989	3.896252
1	1.853164	0.944529	1.972717
6	0.171362	2.265254	4.606734
1	-1.633409	3.438371	4.460256
1	1.951447	1.068798	4.423258
1	-6.041043	-5.064823	-0.522670
1	-0.317921	7.550368	-1.527114
1	0.224450	2.327236	5.690230
1	-0.726522	-1.601918	5.811219
6	4.604663	-2.178132	-1.455508
1	4.556519	-3.257719	-1.287323
1	4.794901	-2.030899	-2.531199
6	5.762112	-1.630059	-0.641439
6	5.601944	-1.309780	0.707885
6	7.017645	-1.479896	-1.230811
6	6.682023	-0.846562	1.454363
1	4.621901	-1.411237	1.166728
6	8.102008	-1.021728	-0.484224
1	7.150381	-1.717000	-2.284883
6	7.935979	-0.702336	0.861657
1	6.543340	-0.593881	2.501885
1	9.073513	-0.907326	-0.956889
1	8.777153	-0.337814	1.444292

2,1-insertion

E (UwB97XD) = −2887.07560587

Zero-point correction = 0.750415 (Hartree/Particle)

Thermal correction to Energy = 0.798657

Thermal correction to Enthalpy = 0.799601

Thermal correction to Gibbs Free Energy = 0.662450

Sum of electronic and zero-point Energies = −2886.325190

Sum of electronic and thermal Energies = −2886.276949

Sum of electronic and thermal Enthalpies = −2886.276005

Sum of electronic and thermal Free Energies = −2886.413156

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	-1.982702	0.761539	-0.796103
1	-2.623624	2.248819	-0.784810
6	-1.635401	0.480214	-2.695220
8	-1.426201	0.335572	-3.821554
6	-4.104949	0.482654	-0.616029
6	-3.843104	1.726442	0.055110
15	-1.574016	-1.428922	0.163059
15	-0.077745	1.968237	-0.017709
1	-4.303885	-0.380096	0.017555
1	-3.761509	1.747334	1.139284
1	-4.309939	2.632282	-0.341554
6	-4.906327	0.491329	-1.893463
1	-4.695621	-0.398389	-2.489913
1	-4.640119	1.374007	-2.494729
8	-6.313210	0.451928	-1.657371
1	-6.533883	1.161678	-1.041188
6	1.607148	1.554565	-0.641909
6	1.996683	0.226835	-0.584584
6	2.483108	2.452905	-1.268796
6	3.161908	-0.268713	-1.175270
6	3.671521	1.993788	-1.825354
1	2.231822	3.505894	-1.333199
6	4.012489	0.639678	-1.801005
1	4.344275	2.698132	-2.305247
1	4.939411	0.309215	-2.255913
8	1.200413	-0.655623	0.104829
6	1.049839	-1.856451	-0.545660
6	-0.206416	-2.437054	-0.553276
6	2.177843	-2.426431	-1.143841
6	-0.324556	-3.708928	-1.130103
6	2.027598	-3.674553	-1.746630

6	0.784754	-4.312542	-1.711956	6	-0.127014	3.766063	-0.429685
1	-1.281591	-4.219365	-1.133362	6	0.481369	4.734035	0.378456
1	2.858952	-4.154754	-2.251498	6	-0.723300	4.167322	-1.629429
1	0.682688	-5.292374	-2.168934	6	0.480106	6.074836	0.001030
7	3.360974	-1.662386	-1.096044	1	0.961855	4.442484	1.308083
6	-2.982903	-2.592610	-0.057548	6	-0.716056	5.507238	-2.012801
6	-3.570148	-3.303613	0.990962	1	-1.196387	3.424867	-2.265566
6	-3.507726	-2.734201	-1.349357	6	-0.118346	6.464867	-1.196287
6	-4.663490	-4.138115	0.752560	1	0.950899	6.814498	0.642783
1	-3.182580	-3.207443	2.000831	1	-1.182265	5.801053	-2.949080
6	-4.589675	-3.573127	-1.588913	6	0.117126	2.028604	1.810684
1	-3.066094	-2.173131	-2.169481	6	-0.900960	2.658301	2.539662
6	-5.174239	-4.276055	-0.534541	6	1.183223	1.453421	2.502155
1	-5.115540	-4.678553	1.579720	6	-0.838291	2.737364	3.925567
1	-4.986990	-3.667079	-2.595573	1	-1.742491	3.103047	2.012895
6	-1.234575	-1.560254	1.963700	6	1.234026	1.510842	3.895421
6	-1.848635	-0.627537	2.802573	1	1.984336	0.957855	1.963511
6	-0.432271	-2.556966	2.527118	6	0.231474	2.158337	4.609669
6	-1.683530	-0.698412	4.182685	1	-1.627924	3.244884	4.473386
1	-2.445826	0.167826	2.364250	1	2.065248	1.047794	4.419797
6	-0.251162	-2.618386	3.907043	1	-0.739923	-1.741731	5.813903
1	0.053064	-3.290486	1.888783	1	0.277638	2.207760	5.694088
6	-0.880950	-1.692644	4.737560	1	-0.118286	7.510720	-1.490831
1	-2.163954	0.036762	4.821298	1	-6.028681	-4.921457	-0.717325
1	0.379566	-3.393722	4.333645	6	4.625782	-2.232823	-1.511755

1	4.807037	-2.078648	-2.588100
1	4.558577	-3.312841	-1.352890
6	5.801355	-1.713066	-0.705403
6	5.662633	-1.409661	0.650248
6	7.051421	-1.572317	-1.308593
6	6.758461	-0.972192	1.389277
1	4.687225	-1.504497	1.120268
6	8.151436	-1.139895	-0.569520
1	7.167735	-1.796819	-2.367346
6	8.006782	-0.837125	0.782633
1	6.636723	-0.732989	2.442051
1	9.118516	-1.032706	-1.052798
1	8.860343	-0.492937	1.359586

L5

1,2-insertion

E (UwB97XD) = −3029.53377971

Zero-point correction = 0.891772 (Hartree/Particle)

Thermal correction to Energy = 0.950040

Thermal correction to Enthalpy = 0.950984

Thermal correction to Gibbs Free Energy = 0.792706

Sum of electronic and zero-point Energies = −3028.642008

Sum of electronic and thermal Energies = −3028.583740

Sum of electronic and thermal Enthalpies = −3028.582795

Sum of electronic and thermal Free Energies = −3028.741073

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z

45	0.182564	-0.934060	-1.490400
1	-0.654154	-1.856706	-2.524013
6	0.261329	0.377866	-2.844759
8	0.306428	1.182948	-3.673699
6	0.592398	-2.911611	-0.623129
6	0.183599	-3.172221	-1.954880
15	1.912815	0.096116	-0.215196
15	-1.868644	-0.394628	-0.138347
1	1.660937	-2.954222	-0.410861
1	-0.056673	-3.186070	0.205070
1	-0.776478	-3.674509	-2.086133
6	1.198265	-3.534368	-3.017048
1	0.863567	-3.222331	-4.008147
1	2.150980	-3.033553	-2.801022
8	1.371577	-4.945193	-3.100078

1	1.666209	-5.259777	-2.235634	1	3.075911	-0.920883	-2.610547
6	-2.407580	1.365512	-0.293636	6	6.149395	-1.408422	-1.265441
6	-3.739705	1.810274	-0.507649	6	1.873536	0.041637	1.623476
6	-1.426484	2.331930	-0.318376	6	1.670164	-1.196105	2.240676
6	-4.030988	3.134712	-0.731730	6	2.100463	1.164512	2.416967
1	-4.545943	1.083231	-0.494901	6	1.730948	-1.329157	3.624477
6	-1.659160	3.687745	-0.636866	1	1.461534	-2.071770	1.635473
6	-2.999589	4.109667	-0.814030	6	2.135157	1.065666	3.812061
1	-5.062502	3.447500	-0.870540	1	2.260453	2.136369	1.956619
6	2.077518	1.900877	-0.540161	6	1.963991	-0.186824	4.396107
6	3.224685	2.568045	-0.962051	6	-3.434412	-1.261461	-0.580613
6	0.898233	2.641220	-0.448339	6	-4.481956	-1.467666	0.328278
6	3.163088	3.924162	-1.295032	6	-3.591767	-1.683090	-1.899034
1	4.162853	2.028065	-1.051374	6	-5.661851	-2.092918	-0.066536
6	0.785775	3.984754	-0.807727	1	-4.375401	-1.135233	1.357923
6	1.959357	4.618130	-1.235031	6	-4.770517	-2.306331	-2.326800
1	4.060112	4.434973	-1.631668	1	-2.784485	-1.520885	-2.610079
1	1.929235	5.658291	-1.545340	6	-5.789517	-2.506051	-1.399117
8	-0.169841	1.946236	0.025682	6	-1.799689	-0.657200	1.679313
6	3.611153	-0.507301	-0.575960	6	-1.859664	-1.967801	2.163668
6	4.632590	-0.532497	0.380501	6	-1.602510	0.387673	2.583677
6	3.878420	-0.936446	-1.874704	6	-1.768687	-2.239105	3.528998
6	5.908424	-0.985131	0.047231	1	-2.017019	-2.793464	1.471510
1	4.431951	-0.201853	1.396618	6	-1.486048	0.142521	3.951976
6	5.150807	-1.389440	-2.238041	1	-1.536831	1.411333	2.226407

6	-1.580135	-1.173121	4.409372
1	7.143498	-1.766533	-1.530721
1	1.999006	-0.278546	5.481247
1	-1.493005	-1.372109	5.477235
1	-6.709778	-2.996086	-1.715036
6	-0.562159	4.586774	-0.801938
6	-0.836912	5.915731	-1.046079
1	-0.031338	6.633162	-1.169747
6	-2.173462	6.361092	-1.164171
1	-2.361025	7.413900	-1.355430
6	-3.229943	5.486084	-1.071991
1	-4.250417	5.838020	-1.198570
6	5.410169	-1.860973	-3.647533
1	6.462836	-2.120895	-3.796583
1	4.808134	-2.747136	-3.880691
1	5.144946	-1.087001	-4.376225
6	7.011977	-1.028754	1.075853
1	6.681232	-0.611491	2.031866
1	7.341739	-2.058815	1.255415
1	7.886795	-0.458794	0.742447
6	2.340461	2.300772	4.653719
1	1.443268	2.931567	4.645796
1	2.556734	2.043719	5.695669
1	3.169730	2.908079	4.274697
6	1.571166	-2.678124	4.277377
1	2.548476	-3.109885	4.526604
1	0.994484	-2.604135	5.205416
1	1.053833	-3.378583	3.614768
6	-4.910675	-2.753192	-3.761136
1	-4.775147	-1.911545	-4.449630
1	-4.154540	-3.505552	-4.013563
1	-5.896232	-3.189883	-3.950548
6	-6.785695	-2.326421	0.913374
1	-7.722346	-1.884330	0.554738
1	-6.964728	-3.398425	1.058020
1	-6.558590	-1.889679	1.890745
6	-1.901550	-3.653335	4.038467
1	-1.381679	-3.785860	4.993030
1	-2.955157	-3.914547	4.196677
1	-1.489233	-4.374968	3.324994
6	-1.274588	1.276314	4.923424
1	-2.155417	1.422244	5.560281
1	-0.419906	1.076136	5.579400
1	-1.080640	2.216308	4.397528

2,1-insertion

E (UwB97XD) = −3029.52532078

Zero-point correction = 0.892323 (Hartree/Particle)

Thermal correction to Energy = 0.949556

Thermal correction to Enthalpy = 0.950500

Thermal correction to Gibbs Free Energy = 0.795218

Sum of electronic and zero-point Energies = −3028.632998

Sum of electronic and thermal Energies = −3028.575765

Sum of electronic and thermal Enthalpies = −3028.574821

Sum of electronic and thermal Free Energies = −3028.730103

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.149564	-1.094409	-1.329916
1	-0.724059	-2.442990	-1.531967
6	0.027856	-0.239347	-3.074882
8	-0.067233	0.238072	-4.122905
6	1.565070	-2.674125	-1.612806
6	0.444322	-3.298609	-0.958196
15	1.839944	0.234179	-0.143688
15	-1.855387	-0.436571	-0.170148
1	2.445296	-2.486978	-0.999795
1	0.470106	-3.466176	0.116657
1	-0.075835	-4.101932	-1.487794
6	1.897326	-3.055200	-3.033266
1	2.438905	-2.251092	-3.535508
1	0.970346	-3.240391	-3.597067
8	2.765677	-4.186602	-3.111531
1	2.385412	-4.893164	-2.574604
6	-2.524945	1.276297	-0.307237
6	-1.606071	2.297775	-0.293078
6	-3.878340	1.639834	-0.537764
6	-1.910929	3.643714	-0.585549
6	-4.243231	2.950078	-0.739392
1	-4.638586	0.865166	-0.558220
6	-3.270851	3.987409	-0.780280
1	-5.288591	3.203799	-0.893773
8	-0.341904	1.966969	0.065803
6	0.693841	2.732822	-0.365119
6	1.908621	2.056361	-0.439876
6	0.514575	4.079332	-0.688611
6	3.030302	2.801903	-0.799480
6	1.663649	4.789352	-1.056768
6	2.904825	4.162680	-1.093458
1	4.001293	2.321224	-0.869272
1	1.586718	5.836285	-1.334737
1	3.784303	4.731508	-1.379711
6	3.572339	-0.207947	-0.573578
6	4.576162	-0.420674	0.371849

6	3.871151	-0.345709	-1.931529	6	-1.640937	-2.388769	3.425293
6	5.867098	-0.780390	-0.026697	1	-1.811174	-2.881417	1.342881
1	4.358389	-0.308674	1.430959	6	-1.508117	-0.009935	3.935765
6	5.147079	-0.711576	-2.356790	1	-1.652466	1.315618	2.255209
1	3.085958	-0.183410	-2.667257	6	-1.520067	-1.342279	4.344248
6	6.133856	-0.921618	-1.389565	1	1.978722	-0.346692	5.526461
6	1.857633	0.134875	1.689393	1	-1.413880	-1.574481	5.403343
6	1.724418	-1.138981	2.247224	1	-6.537198	-3.229096	-1.875976
6	2.019511	1.234812	2.530119	1	7.134958	-1.210326	-1.707423
6	1.793673	-1.331225	3.624479	6	-0.864309	4.606475	-0.705232
1	1.557691	-1.992660	1.593326	6	-1.211864	5.922414	-0.927081
6	2.057017	1.075089	3.918425	1	-0.448215	6.688935	-1.017372
1	2.117922	2.232351	2.108272	6	-2.570248	6.289829	-1.065229
6	1.952572	-0.211476	4.445523	1	-2.815732	7.333798	-1.238635
6	-3.350272	-1.392866	-0.662036	6	-3.576233	5.353514	-1.013903
6	-4.394617	-1.666677	0.231044	1	-4.612502	5.649228	-1.154701
6	-3.475318	-1.782129	-1.993815	6	-1.687677	-3.824791	3.886370
6	-5.543206	-2.331219	-0.192387	1	-1.157076	-3.959851	4.834531
1	-4.311850	-1.358515	1.270368	1	-2.723723	-4.151658	4.038460
6	-4.623335	-2.441510	-2.449049	1	-1.238033	-4.496461	3.147116
1	-2.666303	-1.573144	-2.690011	6	-1.360297	1.109082	4.935581
6	-5.641193	-2.710376	-1.536965	1	-2.339629	1.494286	5.245597
6	-1.772382	-0.745890	1.638428	1	-0.834222	0.770689	5.834405
6	-1.738743	-2.076047	2.071996	1	-0.794171	1.942975	4.508182
6	-1.650723	0.277289	2.575192	6	1.707880	-2.714166	4.216792

1	1.138154	-2.711272	5.152166
1	1.220435	-3.409778	3.526977
1	2.707961	-3.106837	4.438541
6	2.234528	2.269065	4.824239
1	1.725219	2.121183	5.782530
1	3.295823	2.445912	5.038163
1	1.835475	3.179581	4.365213
6	-4.735154	-2.847433	-3.897901
1	-4.678419	-1.972609	-4.555409
1	-3.917756	-3.520092	-4.181406
1	-5.680660	-3.360805	-4.098821
6	-6.662142	-2.643853	0.770892
1	-7.619176	-2.252851	0.406997
1	-6.779047	-3.726478	0.899326
1	-6.472072	-2.208431	1.756710
6	6.943291	-1.041678	0.998755
1	6.711977	-0.555320	1.951773
1	7.044622	-2.116880	1.191150
1	7.917513	-0.675865	0.657168
6	5.430313	-0.932557	-3.821180
1	6.485552	-0.760844	-4.057527
1	5.188131	-1.965091	-4.101595
1	4.826172	-0.269209	-4.448525

L6

1,2-insertion

E (UwB97XD) = −2931.27333960

Zero-point correction = 0.861602 (Hartree/Particle)

Thermal correction to Energy = 0.917974

Thermal correction to Enthalpy = 0.918918

Thermal correction to Gibbs Free Energy = 0.765763

Sum of electronic and zero-point Energies = −2930.411738

Sum of electronic and thermal Energies = −2930.355366

Sum of electronic and thermal Enthalpies = −2930.354422

Sum of electronic and thermal Free Energies = −2930.507577

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z

45	-0.191012	-1.658810	-0.344934
1	0.790685	-2.810969	-0.943287
6	-0.407438	-2.669643	1.230074
8	-0.531109	-3.273966	2.208629
6	-0.532521	-1.294212	-2.511251
6	0.243381	-2.467668	-2.496360

15	-1.900345	-0.120388	0.208495	6	-2.182955	-0.113136	4.843863
15	1.892240	-0.268759	0.031902	1	-4.280696	-0.506489	4.613400
1	-1.603348	-1.389799	-2.679154	1	-2.202109	-0.201873	5.927270
1	-0.085264	-0.358125	-2.830061	8	0.159008	0.631763	2.158487
1	1.293020	-2.373348	-2.779877	7	0.254489	0.333074	4.830662
6	-0.349370	-3.839927	-2.776687	1	0.273016	0.049105	5.800896
1	-0.565233	-3.918704	-3.848531	6	-3.602849	-0.485407	-0.374649
1	0.393086	-4.611180	-2.523973	6	-4.614901	0.483280	-0.334927
8	-1.563739	-4.072474	-2.106293	6	-3.887989	-1.750899	-0.874874
1	-1.436689	-3.712122	-1.204657	6	-5.899028	0.189339	-0.785052
6	2.306354	-0.308963	1.826304	1	-4.394303	1.479948	0.041616
6	3.500718	-0.772869	2.392428	6	-5.168807	-2.074816	-1.337509
6	1.297164	0.078908	2.696079	1	-3.096352	-2.490604	-0.928810
6	3.628292	-0.866636	3.776304	6	-6.156908	-1.094371	-1.285039
1	4.324243	-1.069306	1.750610	1	-7.156887	-1.327077	-1.650391
6	1.387265	-0.040908	4.081743	6	-1.700894	1.597711	-0.419930
6	2.574925	-0.521023	4.625405	6	-1.948926	1.814380	-1.779675
1	4.557157	-1.230692	4.205312	6	-1.298515	2.668796	0.374597
1	2.678319	-0.624317	5.702748	6	-1.824392	3.082762	-2.342046
6	-2.137493	0.047633	2.029470	1	-2.272015	0.988362	-2.409379
6	-3.332260	-0.227640	2.708001	6	-1.145517	3.946783	-0.168907
6	-1.004632	0.277764	2.798850	1	-1.086392	2.522974	1.428345
6	-3.349651	-0.289169	4.098682	6	-1.417879	4.137956	-1.522314
1	-4.241912	-0.417461	2.148526	1	-1.298297	5.131320	-1.953416
6	-0.987982	0.167200	4.189369	6	3.455318	-0.917130	-0.700043

6	4.459453	-0.098868	-1.215834	6	-2.150806	3.308894	-3.797856
6	3.631907	-2.307564	-0.729113	1	-3.227749	3.464004	-3.936871
6	5.624871	-0.646567	-1.766040	1	-1.635959	4.191365	-4.191554
1	4.345110	0.981970	-1.193705	1	-1.863248	2.446955	-4.409618
6	4.787690	-2.878407	-1.255726	6	-0.709029	5.094701	0.706010
1	2.855751	-2.951803	-0.322013	1	-0.024008	4.752142	1.488094
6	5.773799	-2.031582	-1.776359	1	-0.195030	5.865126	0.121647
1	6.678237	-2.467956	-2.198754	1	-1.569418	5.565913	1.197409
6	2.020562	1.522153	-0.358591	6	1.448225	3.644099	-3.475943
6	1.680319	1.911945	-1.656844	1	0.918239	4.602452	-3.498234
6	2.441391	2.491530	0.551232	1	2.357453	3.753906	-4.079907
6	1.783779	3.239906	-2.063174	1	0.811768	2.897060	-3.960154
1	1.328964	1.166595	-2.366185	6	3.001534	4.875159	1.166187
6	2.534570	3.834913	0.177551	1	4.087185	5.018923	1.102303
1	2.704156	2.205709	1.566816	1	2.528931	5.845003	0.977149
6	2.209338	4.189672	-1.131102	1	2.768681	4.579044	2.194273
1	2.271726	5.235653	-1.430278	6	6.684730	0.259870	-2.343026
6	-6.995060	1.226357	-0.749023	1	7.614306	-0.283954	-2.538678
1	-6.628790	2.179027	-0.354315	1	6.348881	0.700179	-3.289547
1	-7.397318	1.409787	-1.752112	1	6.911889	1.086643	-1.661182
1	-7.828931	0.898066	-0.117586	6	4.978891	-4.375219	-1.273777
6	-5.454930	-3.458439	-1.865772	1	5.865211	-4.666475	-0.698117
1	-4.550581	-3.912892	-2.282277	1	4.115095	-4.891837	-0.844462
1	-5.813587	-4.113335	-1.062069	1	5.118359	-4.743375	-2.296885
1	-6.225421	-3.437848	-2.643764	----------			

2,1-insertion

E (UwB97XD) = −2931.26245394

Zero-point correction = 0.861274 (Hartree/Particle)

Thermal correction to Energy = 0.917173

Thermal correction to Enthalpy = 0.918117

Thermal correction to Gibbs Free Energy = 0.765448

Sum of electronic and zero-point Energies = −2930.401180

Sum of electronic and thermal Energies = −2930.345281

Sum of electronic and thermal Enthalpies = −2930.344337

Sum of electronic and thermal Free Energies = −2930.497006

Standard orientation:

Atomic Number	Coordinates (Angstroms) X	Y	Z
45	0.033962	-1.560512	-0.391673
1	1.079976	-2.152589	-1.477071
6	0.003509	-2.957133	0.966677
8	0.015928	-3.793877	1.763312
6	-1.157169	-2.344919	-1.993786
6	0.055276	-1.894856	-2.625222
15	-1.775362	-0.068853	0.271374
15	1.936365	-0.217595	0.150192
1	-2.038544	-1.719780	-2.126968
1	0.082024	-0.923960	-3.115394
1	0.669563	-2.636475	-3.143688
6	-1.466973	-3.820203	-1.960864
1	-2.124385	-4.062834	-1.123779
1	-0.536122	-4.394072	-1.835266
8	-2.174168	-4.260563	-3.121110
1	-1.692330	-3.954079	-3.899585
6	2.355831	0.139914	1.913264
6	1.328691	0.597368	2.722504
6	3.577992	-0.155165	2.535111
6	1.422399	0.691705	4.111754
6	3.713920	-0.014373	3.913359
1	4.416754	-0.511471	1.947156
6	2.639732	0.386408	4.710637
1	4.665222	-0.246099	4.382987
1	2.749183	0.455285	5.790142
8	0.157299	0.984006	2.119553
6	-0.967935	0.606650	2.810322
6	-2.059067	0.174867	2.076173
6	-0.957918	0.697676	4.201489
6	-3.239464	-0.099231	2.779436
6	-2.132976	0.403066	4.885801

6	-3.269438	0.025961	4.166423	6	4.639954	-0.132261	-0.729710
1	-4.127928	-0.418979	2.245227	6	3.687923	-2.322205	-0.407245
1	-2.163362	0.467258	5.970706	6	5.865520	-0.697984	-1.072403
1	-4.187951	-0.191535	4.703344	1	4.539829	0.950159	-0.715188
7	0.257611	1.074965	4.804547	6	4.911075	-2.917804	-0.738281
1	0.295637	0.947685	5.806876	1	2.839468	-2.951007	-0.147947
6	-3.445374	-0.648393	-0.237411	6	5.983621	-2.093587	-1.070235
6	-4.394850	0.173444	-0.846214	1	6.939961	-2.543720	-1.334277
6	-3.748640	-1.993699	-0.014797	6	1.953407	1.415629	-0.690937
6	-5.633597	-0.338788	-1.242095	6	2.108020	1.412061	-2.082679
1	-4.172755	1.222812	-1.021896	6	1.738457	2.624555	-0.035443
6	-4.970333	-2.534804	-0.412454	6	2.099297	2.598079	-2.810846
1	-3.005691	-2.634778	0.455095	1	2.257877	0.468373	-2.604620
6	-5.901400	-1.691615	-1.024225	6	1.680159	3.825803	-0.749157
1	-6.856838	-2.102611	-1.348075	1	1.592748	2.648772	1.039922
6	-1.749070	1.648736	-0.375401	6	1.876044	3.797719	-2.127973
6	-1.428372	1.802144	-1.726572	1	1.836389	4.730025	-2.690193
6	-2.047493	2.775863	0.387521	6	7.046069	0.166076	-1.442832
6	-1.439477	3.056702	-2.329987	1	7.923068	-0.078211	-0.832651
1	-1.157097	0.926450	-2.312830	1	7.326721	0.018631	-2.492479
6	-2.030923	4.051592	-0.183902	1	6.821640	1.227838	-1.302442
1	-2.292238	2.670743	1.441837	6	5.041724	-4.421013	-0.741083
6	-1.734368	4.171954	-1.540792	1	4.717042	-4.845892	0.215091
1	-1.715664	5.162188	-1.995137	1	4.416793	-4.866864	-1.523693
6	3.540672	-0.937109	-0.402547	1	6.075721	-4.733380	-0.917986

6	2.346239	2.587723	-4.299379
1	1.847202	3.426872	-4.795158
1	3.418554	2.666194	-4.517135
1	1.986048	1.660251	-4.757449
6	1.418960	5.122205	-0.024596
1	2.339881	5.520078	0.419511
1	1.019058	5.882848	-0.703227
1	0.695192	4.977412	0.784084
6	-2.352537	5.268135	0.649347
1	-1.849114	6.160475	0.262458
1	-3.430653	5.470603	0.650090
1	-2.043913	5.128999	1.690758
6	-1.147771	3.210680	-3.800393
1	-0.543587	4.103627	-3.993527
1	-0.602491	2.344707	-4.187905
1	-2.076987	3.307467	-4.375464
6	-6.669218	0.556136	-1.878288
1	-7.436675	0.845759	-1.150021
1	-6.216956	1.474283	-2.266270
1	-7.177047	0.050828	-2.706888
6	-5.242940	-4.008243	-0.244225
1	-6.315779	-4.213343	-0.168893
1	-4.854938	-4.565563	-1.105753
1	-4.754730	-4.403702	0.652425

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